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### REMARKS

Applicants and Applicants' attorney would like to thank Examiner Dang for his patience and guidance in the interview of May 25, 2004. Claims 28-32, previously withdrawn in the restriction requirement, are cancelled herewith. Pending claims now include Claims 1-27.

### Rejections Under 35 USC § 103

The current application has been assigned to RJLee Group, Inc., and the assignment recorded in the United States Patent and Trademark Office, Assignment Division, at Reel/Frame 014700/0719. Thus, all claims were commonly owned at the time the invention was made.

Claims 1-26 were rejected under 35 USC § 103(a) as being unpatentable over Gi (4,463,203) in view of either Roy (4,740,270) or Solbakken et al. (4,250,158). Claim 1 has been amended to recite "clay catalyst and elemental metal dust catalyst" to clearly indicate that two catalytic substances are added to the pyrolysis chamber. Claim 1 has also been amended to indicate that carbon black is one of the reaction products. The combination of references cited does not teach or suggest the invention recited in Claim 1.

As requested by the Examiner, Applicants submit herewith the following references 1) pages from Volume 4 of the Kirk-Othmer Encyclopedia of Chemical Terminology, 4<sup>th</sup> Ed., Wiley & Sons, 1998; and 2) pages from Volume 6 of the Kirk-Othmer Encyclopedia of Chemical Terminology, 4<sup>th</sup> Ed., Wiley & Sons, 1998.

Reference (1) provides a complete description of carbon black, and describes on page 1037 distinctions that can be made between carbon black and other forms of carbon such as diamond, graphite, coke, and charcoal: carbon blacks are distinct because they are "particulate, composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions". Applicants' method releases carbon black from the rubber tires, whereas the method of Gi produces coke.

Reference (2) provides a complete description of clays, and provides support for Applicants' position that metals in elemental form are not found in clay. See, for example, page 381, first paragraph, which states that clays are composed of hydrous silicates of Al, Mg, K and Fe. At page 386, second full paragraph, this text indicates that these metals are in the cationic form. Thus, the metal dust added by Applicants as an additional catalyst, which is in elemental form, has no relationship to the metals in clay as disclosed by Gi.

Claim 27 was rejected under 35 USC § 103(a) as being unpatentable over Gi (4,463,203) in view of either Roy (4,740,270) or Solbakken et al. (4,250,158), in view of Cha, et al. (4,938,278). Claim 27 relies on Claim 1 for patentability.

Applicants respectfully submit that Claim 1 and the claims depending therefrom are patentable over the Gi reference, alone or in combination with Roy or Solbakken. As all outstanding issues have been addressed, Applicants submit that Claims 1-27 are in condition for allowance; such action is respectfully requested at an early date.

Respectfully submitted,

A handwritten signature in black ink, appearing to read "Debra Z. Anderson", written in a cursive style.

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KIRK-OTHMER

# ENCYCLOPEDIA OF **CHEMICAL** **TECHNOLOGY**

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VOLUME 4

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## CARBON BLACK

Carbon black is a generic term for an important family of products used principally for the reinforcement of rubber, as a black pigment, and for its electrically conductive properties. It is a fluffy powder of extreme fineness and high surface area, composed essentially of elemental carbon. Plants for the manufacture of carbon black are strategically located worldwide in order to supply the rubber tire industry, which consumes 70% of production. About 20% is used for other rubber products and 10% is used for special nonrubber applications. World capacity in 1988 was estimated at over six million metric tons; U.S. capacity was almost 1.6 million metric tons. Carbon black was ranked 38 in 1989 among the 50 largest volume industrial chemicals produced in the United States. Six U.S. manufacturers (1) were operating 22 plants in 1990. Many of these are located in the south and southwest. Over 35 grades, listed in ASTM 1765-87 (2), are used by the rubber industry, and one manufacturer supplies an additional 45 grades for special pigment applications.

Carbon blacks differ from other forms of bulk carbon such as diamond, graphite, cokes, and charcoal in that they are particulate, composed of aggregates having complex configurations, quasigraphitic in structure, and of colloidal dimensions. They differ from other bulk carbons in having their origin in the vapor phase through the thermal decomposition and the partial combustion of hydrocarbons. Carbon black is a product of a process incorporating the latest engineering technology and process controls. Its purity differentiates it from soots that are impure by-products from the combustion of coal and oils and from the use of diesel fuels. Carbon blacks are essentially free of the inorganic contaminants and extractable organic residues characteristic of most forms of soot.

A number of processes have been used to produce carbon black including the oil-furnace, impingement (channel), lampblack, and the thermal decomposition of natural gas and acetylene (3). These processes produce different grades of carbon

and are referred to by the process by which they are made, eg, oil-furnace black, lampblack, thermal black, acetylene black, and channel-type impingement black. A small amount of by-product carbon from the manufacture of synthesis gas from liquid hydrocarbons has found applications in electrically conductive compositions. The different grades from the various processes have certain unique characteristics, but it is now possible to produce reasonable approximations of most of these grades by the oil-furnace process. Since over 95% of the total output of carbon black is produced by the oil-furnace process, this article emphasizes this process.

### History of Carbon Black Manufacture

The use of carbon black as a pigment dates back to prehistoric times. Cave wall dwellings and objects from ancient Egypt were decorated with paints and lacquers containing carbon black. The oldest process practiced in China about 3000 BC consisted of the partial combustion of vegetable oils in small lamps with ceramic covers. The smoke impinged on the covers from which the adhering carbon black was carefully removed. Another old process is the lampblack process, which is the ancestor of all modern carbon blacks. Until the 1870s it was the only commercial process, and because of this the word lampblack is occasionally used as a generic term for carbon black. In the lampblack process, oils are burned in open, shallow pans in a restricted air supply. The heavy, carbon-laden smoke is passed through a series of settling chambers and filters from which the flocculated carbon deposits are recovered.

Prior to 1870 it was already known that carbon black with much higher covering power and jetness could be recovered from underventilated illuminating gas flames impinging on a cold surface. These gas blacks led to the development of the channel process, the name deriving from the iron channels used for the collection of the carbon blacks from the impingement of thousands of small luminous flames burning in a restricted atmosphere of air. This process dominated the industry for over 50 years. In 1926 there were 33 producers in the United States. Because of poor carbon yields from natural gas in the range of 1-5% and severe atmospheric pollution, this process has become extinct. The last channel black plant in the United States was closed in 1976.

In the 1920s two other processes using natural gas were introduced that gave much higher yields with large decreases in atmospheric contamination. One was the cyclic thermal black process. Alternate heating and production cycles in large brick checkered chambers are used to produce a unique large particle size, essentially unaggregated-grade useful for many special rubber and plastic applications. Thermal black is produced in the United States, Canada, England, and a few other locations worldwide. The other process, based on natural gas, was the so-called gas-furnace process and is no longer used. This process was continuous and the forerunner of the oil-furnace process. It was discontinued because of the relatively low yield, high raw material cost, and limited range of products.

The first commercial oil-furnace process was put into operation in 1943 by the Phillips Petroleum Co. in Borger, Texas. The oil-furnace blacks rapidly displaced all other types used for the reinforcement of rubber and today account

for practically all carbon black production. In the oil-furnace process heavy aromatic residual oils are atomized into a primary combustion flame where the excess oxygen in the primary zone burns a portion of the residual oil to maintain flame temperatures, and the remaining oil is thermally decomposed into carbon and hydrogen. Yields in this process are in the range of 35 to 50% based on the total carbon input. A broad range of product qualities can be produced.

Before World War I carbon black was almost exclusively used as a black pigment for printing inks, paints, and enamels. The singular event that changed the industry from a small specialty product manufacturer to large volume producer of a vital raw material was the discovery of rubber reinforcement in 1904 (4). The automobile and the tire industries were expanding rapidly, and there was a demand for longer wearing automobile tires. The use of carbon black as a filler for rubber fulfilled this need providing longer wearing and more durable pneumatic tires. The use of carbon black in tires remains its most important application, coupling the fortunes of the carbon black industry to that of the automotive industry.

### Physical Structure of Carbon Black

**Molecular and Crystallite Structure.** The arrangement of carbon atoms in carbon black has been well-established by x-ray diffraction methods (5,6). The diffraction patterns show diffuse rings at the same positions as diffraction rings from pure graphite. The suggested relation to graphite is further emphasized as carbon black is heated to 3000°C. The diffuse reflections sharpen, but the pattern never achieves that of true graphite. Carbon black can have a degenerated graphitic crystallite structure. Whereas graphite has three-dimensional order, as seen in the model structures of Figure 1, carbon black has two-dimensional order. The x-ray data indicate that carbon black consists of well-developed graphite platelets stacked roughly parallel to one another but random in orientation with respect to adjacent layers. As shown in Figure 1 the carbon atoms in the graphite structure form large sheets of condensed aromatic ring systems with an interatomic spacing of 0.142 nm, comparable to the aromatic carbon separation distance of 0.139 nm in benzene. The large graphite interplanar distance of 0.335 nm results in a specific gravity of 2.26. In carbon black the interplanar distance is still larger, in the range of 0.350–0.365 nm, as a consequence of the random planar orientations or so-called turbostratic arrangement. The specific gravities of commercial carbon blacks are 1.76–1.90 depending on the grade. X-ray diffraction data provide estimates of crystallite size.  $L_a$  is the average layer plane diameter and  $L_c$  is the average crystallite thickness. For a typical carbon black  $L_a$  is 1.7 nm and  $L_c$  is 1.5 nm, which corresponds to an average of four layer planes per crystallite containing 375 carbon atoms. A particle of a 100 m<sup>2</sup>/g carbon black contains over 4000 crystallites. It was originally suggested that these discrete crystallites were in random orientation within the particle. This view was later abandoned when electron microscopy of graphitized and oxidized carbon blacks indicated more of a concentric layer plane arrangement. This structure has been confirmed by the use of high resolution phase-contrast electron microscopy that made possible the direct imaging of graphitic layer planes in carbon black (7).

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Figure 2 shows a phase-contrast electron micrograph of carbon black at high resolution that displays the marked concentric arrangement of the layer planes at the surface and around what appear to be growth centers.

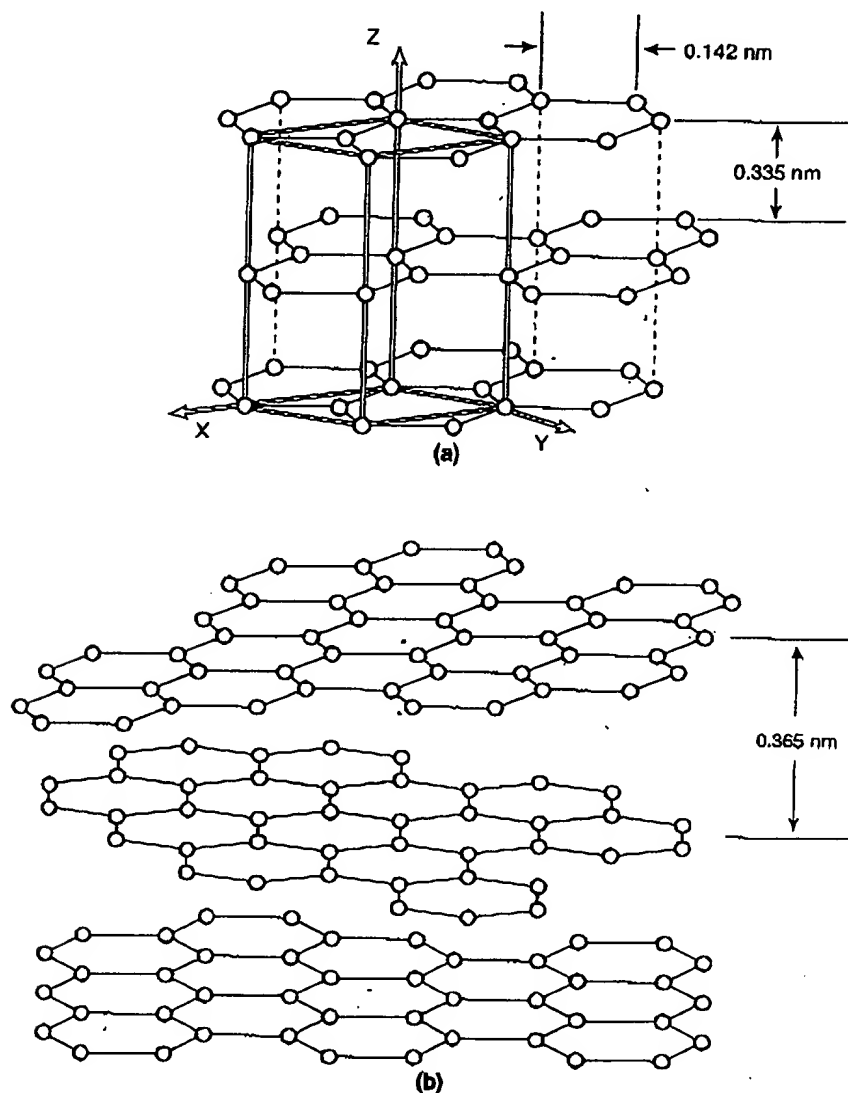


Fig. 1. Atomic structural models of (a), graphite, and (b), carbon black.

The word particle has become so widely used in the technical rubber and carbon black literature that it is convenient to retain the term when in fact nodule is meant. The layer planes are curved, distorted, and of varying size. They also intersect and interconnect one particle or nodule with its neighbors. This type of structure has been termed paracrystalline. It is obvious that individual particles do not exist in carbon blacks, with the exception of thermal blacks, and that the functional unit is an aggregate of nodules that probably existed as smaller particles at some early stage of the carbon formation process. The functional unit in well-dispersed systems is called an aggregate.

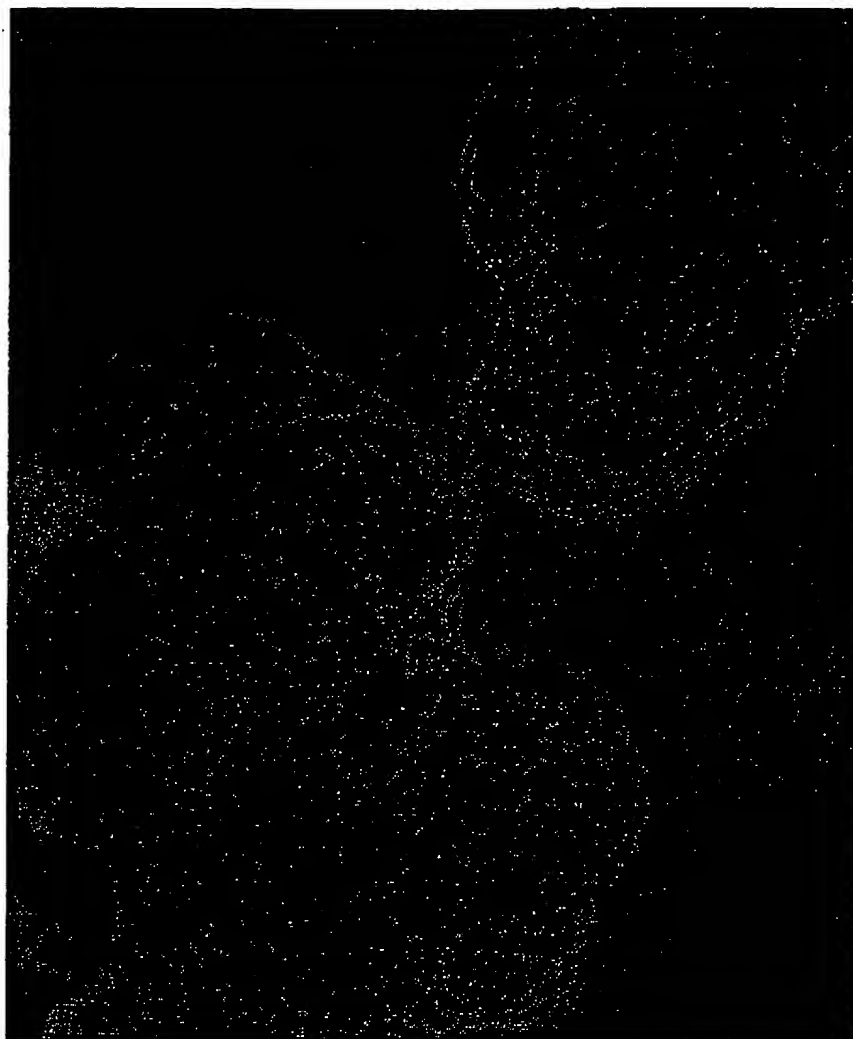


Fig. 2. High resolution (3,000,000  $\times$ ) electron micrograph of H-300-grade carbon black. Courtesy of W. M. Hess.

**Morphology.** In describing carbon black, three terms are used to describe structures of increasing scale and complexity:

*Particles* (nodules) are the primary structure element. They are roughly spherical elements that are joined in the aggregate structures.

*Aggregates* are the primary dispersable elements of carbon black in all but thermal blacks. The particles in an aggregate are connected and have grown together.

*Agglomerates* are undispersed clusters of aggregates held together by van der Waals forces or by binders. The term structure is used to describe both the extent and the complexity with which the particles are interconnected in aggregates. Primary measures of structure focus on the internal space within the aggregate.

Size and shape of the aggregates in composite systems are the principal features that determine the performance of carbon black as a reinforcing agent and as a pigment (8). Figure 3 shows an electron micrograph of a reinforcing tread black. There is an enormous range in aggregate size. The aggregate size distribution curve for N220 shown in Figure 4 is log-normal, and the range of  $D_e$ , equivalent diameters of the projected areas of the aggregates is about tenfold. Within each aggregate the nodules, or particles, appear to be about the same size. The size of the aggregates is directly related to the size of the particles. The shapes of the aggregates have infinite variety from tight grapelike clusters to open dendritic or branched arrangements to fibrous configurations.

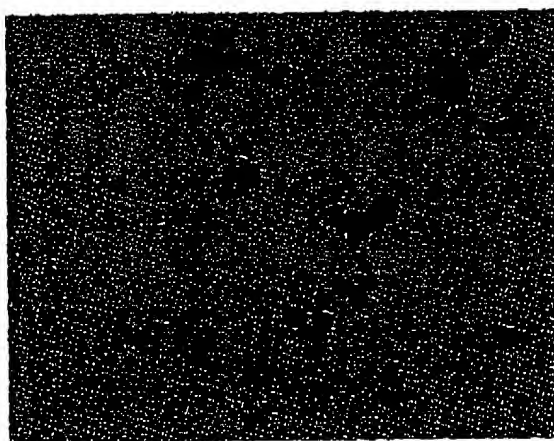


Fig. 3. Electron micrograph of reinforcing-grade of N399 tread black (100,000  $\times$ ).

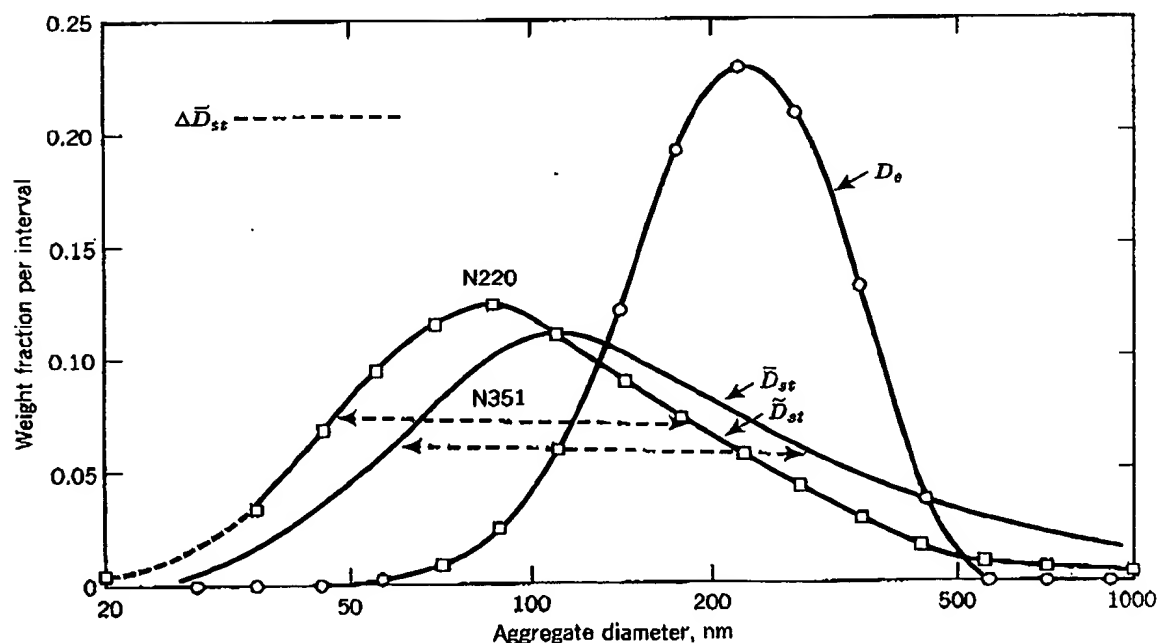


Fig. 4. Aggregate size distributions by electron microscope image analysis ( $D_e$ ) and centrifugal ( $\bar{D}_{st}$ ) sedimentations for N220 and N351 carbon blacks (8).

A useful method for determining relative aggregate sizes and distributions is by centrifugal sedimentation. From the sedimentation rates of the aggregates the Stokes diameter is derived. A convenient instrument for these measurements is the Joyce Loebel disk photosedimentometer (9). Large aggregates sediment at a faster rate than smaller ones. The sedimentation rate is also influenced by the bulkiness of the aggregates. At constant volume or mass, a bulky aggregate sediments more slowly than a compact aggregate because of frictional drag. Figure 4 (8) shows a comparison of a Stokes diameter distribution  $\bar{D}_{St}$  and equivalent diameter distribution  $D_e$  from electron microscopy for N220. In this example the modal  $\bar{D}_{St}$  value is about one-third of the modal  $D_e$  value.

Table 1 lists average  $\bar{D}_{St}$  values from a number of literature sources. This table also lists  $d_{wm}$  values for the aggregates calculated from their estimated volumes. In this case there is reasonable agreement between the two diameters. Aggregate size distributions from centrifugal sedimentation analysis are very useful for assessing the differences in this characteristic within a given grade or at constant surface area. It has been shown that the hysteresis of rubber vulcanizates can be reduced by broadening the aggregate size distribution curve without any significant loss in abrasion resistance (11,12). As shown in Figure 4 this broadening is usually expressed as  $\Delta D_{50}$ , the width at 50% of the modal value.  $\bar{D}_{St}$  values have been related to the dynamic and mechanical performance of rubber-grade carbon blacks. Hysteresis decreases and abrasion loss increases with increasing values of  $\bar{D}_{St}$  (13).

**Table 1. Carbon Black Morphology<sup>a</sup>**

ASTM designation	Particle size, $d_{wm}^b$ , nm	Aggregate size, $d_{wm}^b$ , nm	$\bar{D}_{St}^c$ , nm	Surface area, m <sup>2</sup> /g
N110	27	93	76-111	143
N220	32	103	95-117	117
N234	31	109	74-97	120
N326	41	108	98	94
N330	46	146	116-145	80
N339	39	122	96-125	96
N351	50	159	127	75
N375	36	106	91	105
N550	93	240	220-242	41
N660	109	252	227-283	34
N774	124	265	261	30
N990	403	593	436	9

<sup>a</sup>Ref. 10. Particle size, aggregate size, and surface area are by em.

<sup>b</sup> $d_{wm}$  = weight mean diameter =  $\frac{\sum nd^4}{\sum nd^3}$ .

<sup>c</sup>Stokes diameter by centrifugal sedimentation from various sources.

The tinting strength of rubber-grade carbon blacks shows a linear relationship with  $\bar{D}_{St}$  shown in Figure 5. Since performance characteristics are known to

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depend on aggregate volume, surface area, and bulkiness, it appears that the  $\tilde{D}_{St}$  values combine the effects of all these factors. As such, it is a valuable addition to carbon black characterization methodology.

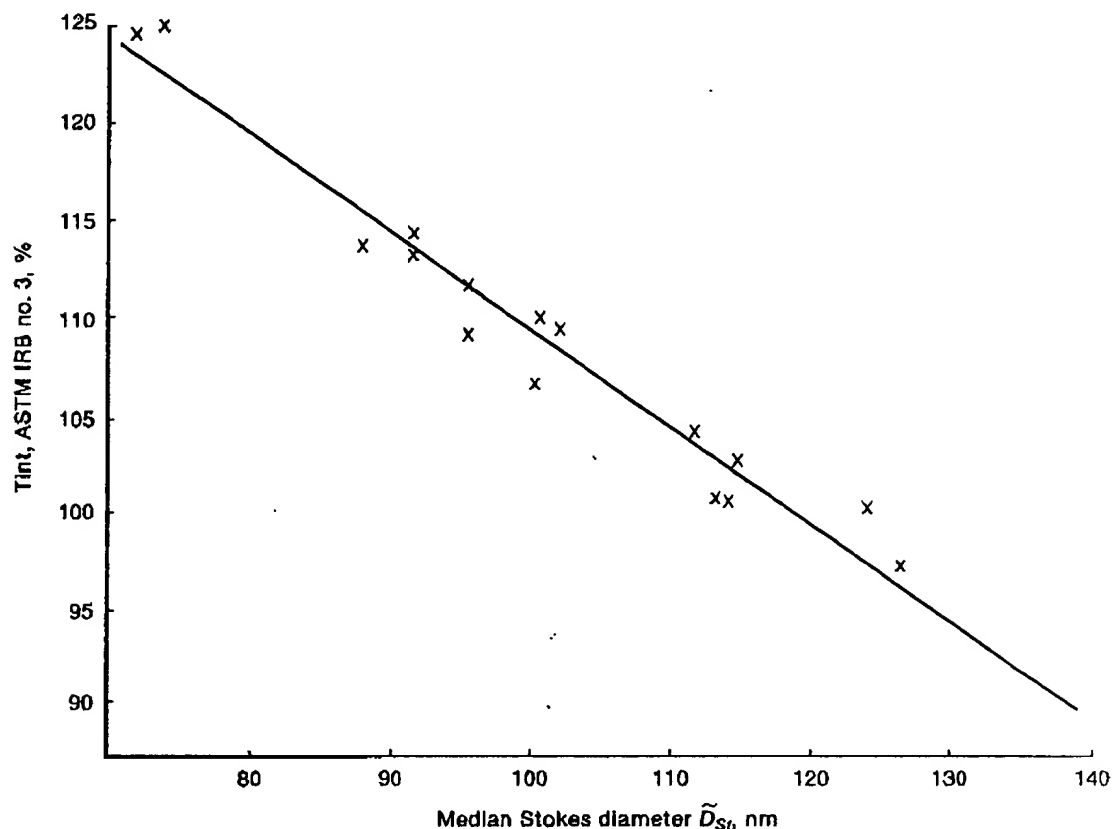


Fig. 5. Tinting strength versus median Stokes diameters for a range of reinforcing tread blacks.

**Aggregate Morphology and Structure.** The term structure is widely used in the carbon black and rubber industries. It was originally introduced in 1944 (14) to describe a chaining tendency of the carbon black particles. It is now used to describe the relative void volume characteristics of grades of black of the same surface area. Structure comparisons of grades with different surface areas cannot be made. It is now known that the properties associated with structure are associated principally with the bulkiness of individual aggregates. Aggregates of the same volume, surface area, and number of nodules have high structure in the open bulky and filamentous arrangement and a low structure in a more clustered compact arrangement.

High structure blacks in unvulcanized rubber give higher Mooney viscosities, lower die swell, faster extrusion rates, and better and more rapid dispersion after incorporation. In vulcanized rubber higher modulus is obtained. High structure blacks give lower bulk densities and high vehicle demand in paint systems.

Structure is usually measured by a void volume test such as the absorption



of dibutyl phthalate (DBPA) (15), or by bulk density measurements of the carbon black under compression. In order to eliminate the effects of pelletizing conditions the DBPA test has been modified to use a sample that has been pre-compressed at a pressure of 165 MPa (24,000 psi) and then broken up four successive times (24M4) (16). This procedure causes some aggregate breakdown and is claimed to more closely approximate the actual breakdown that occurs during rubber mixing.

**Aggregate Breakdown.** Aggregate size analysis by the electron microscope and centrifuge methods are performed on predispersed samples of carbon black. High shear energy, usually ultrasonic, and enough time are employed in these sample preparations to break down microagglomerates to their ultimate aggregates for measurement. When mixed into elastomers under high shear conditions the aggregates themselves undergo fracture forming smaller aggregates that become the actual functional units (17-19). The extent of breakdown depends on shearing stress, energy input, and the grade of carbon black. Elastomer mixes were studied using the techniques of ultramicrotome and automated image analysis. Ultrasonic dispersions of carbon gel preparations from elastomer mixes have also been used in breakdown studies. A high DBPA reinforcing tread grade (N347) exhibited a significant reduction in aggregate length in a BR/OEP tread formulation, whereas a low DBPA grade (N326) showed no measurable change. The extent of aggregate length reduction was 30 to 40% for the normal and high DBPA grades (20).

The effect of elastomer viscosity on aggregate breakdown has been shown (19). A high DBPA grade (N339) was well-mixed with a 52 and a 100 Mooney viscosity OE-SBR. A 43% reduction in aggregate volume was reported for the 52 Mooney rubber and a 53% reduction for 100 Mooney rubber. High resolution electron micrographs show actual fracture locations at the ends of aggregates. The extent of fracture from aggregate length and volume breakdown is consistent with one average fracture per aggregate for the high DBPA grades.

### Chemical Composition

Oil-furnace blacks used by the rubber industry contain over 97% elemental carbon. Thermal and acetylene black consist of over 99% carbon. The ultimate analysis of rubber-grade blacks is shown in Table 2. The elements other than carbon in furnace black are hydrogen, oxygen, and sulfur, and there are mineral oxides and salts and traces of adsorbed hydrocarbons. The oxygen content is located on the surface of the aggregates as  $C_xO_y$  complexes. The hydrogen and sulfur are distributed on the surface and the interior of the aggregates. Some special blacks used for pigment purposes contain larger quantities of oxygen than normal furnace blacks. These blacks are made by oxidation in a separate process step using nitric acid, ozone, air, and other oxidizing agents. They may contain from 2 to 6% oxygen. Oxidation improves dispersion and flow characteristics in pigment vehicle systems such as lithographic inks, paints, and enamels. In rubber-grade blacks surface oxidation reduces pH and changes the kinetics of vulcanization, making the rubber compounds less scorchy and slower curing.

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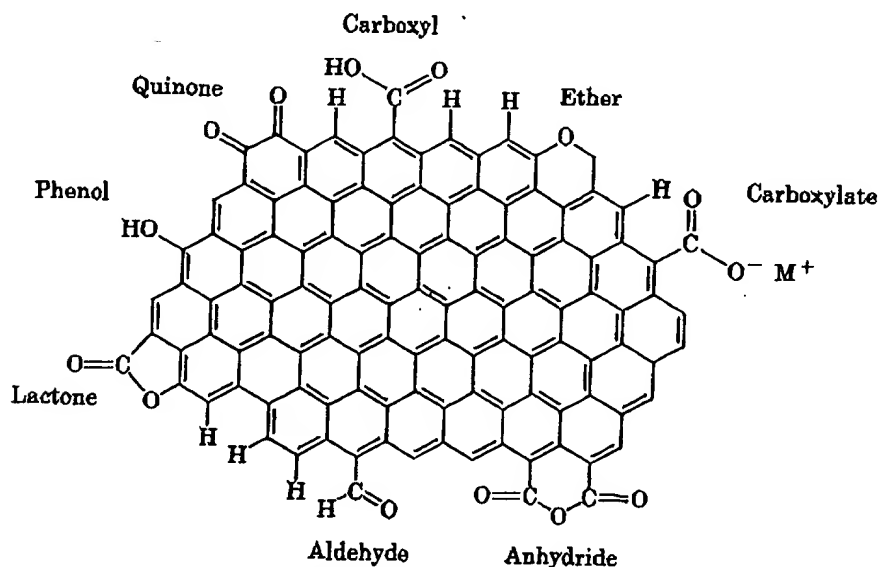
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**Table 2. Chemical Composition of Carbon Blacks, %**

Type	Carbon	Hydrogen	Oxygen	Sulfur	Ash	Volatile
rubber-grade furnace	97.3-99.3	0.20-0.40	0.20-1.20	0.20-1.20	0.10-1.00	0.60-1.50
medium thermal	99.4	0.30-0.50	0.00-0.12	0.00-0.25	0.20-0.38	
acetylene	99.8	0.05-0.10	0.10-0.15	0.02-0.05	0.00	<0.40

A convenient method for assessing the extent of surface oxidation is the measurement of volatile content. This standard method measures the weight loss of the evolved gases on heating up to 950°C in an inert atmosphere. The composition of these gases consists of three principal components: hydrogen, carbon monoxide, and carbon dioxide. The volatile content of normal furnace blacks is under 1.5%, and the volatile content of oxidized special grades is 2.0 to 9.5%.

The origin of the volatile gases is the functional groups attached to the carbon black layer planes. These groups are carbon-bound hydrogen, phenols, hydroquinones, quinones, neutral groups with one oxygen, carboxylic acids, lactones, and neutral groups containing two oxygens (21). Hydrogen is the most dominant of these groups. The oxygen content is present mainly as weakly acidic phenolic groups located at the surface of the aggregates. Figure 6 shows an idealized graphite surface layer plane with the various functional groups located at the periphery of the plane.

**Fig. 6.** Aromatic layer plane with functional side groups.

In addition to combined hydrogen and oxygen, carbon blacks may contain as much as 1.2% combined sulfur resulting from the sulfur content of the aromatic feedstock that contains thiophenes, mercaptans, and sulfides. The combined sulfur appears to be inert and does not contribute to sulfur cross-linking during the vulcanization of rubber compounds.

The ash content of furnace blacks is normally a few tenths of a percent but in some products may be as high as one percent. The chief sources of ash are the water used to quench the hot black from the reactors during manufacture and for wet pelletizing the black. The hardness of the water, and the amount used determines the ash content of the products. The ash consists principally of the salts and oxides of calcium, magnesium, and sodium and accounts for the basic pH (8-10) commonly found in furnace blacks. In some products potassium, in small amounts, is present in the ash content. Potassium salts are used in most carbon black manufacture to control structure and rubber vulcanizate modulus (22). The basic mineral salts and oxides have a slight accelerating effect on the vulcanization reaction in rubber.

### Carbon Black Formation Mechanisms

The formation of carbon black in a candle flame was the subject of a series of lectures in the 1860s by Michael Faraday at the Royal Institution in London (23). Faraday described the nature of the diffusion flame, the products of combustion, the decomposition of the paraffin wax to form hydrogen and carbon, the luminosity of the flame because of incandescent carbon particles, and the destructive oxidation of the carbon by the air surrounding the flame. Since Faraday's time, many theories have been proposed to account for carbon formation in a diffusion flame, but controversy still exists regarding the mechanism (24).

Mechanisms of formation must account for the unique morphology and microstructure of carbon black. These features include the presence of nodules, or particles, multiple growth centers within some nodules, the fusion of nodules into large aggregates, and the paracrystalline or concentric layer plane structure of the aggregates. One mechanism of formation involves the decomposition of the aromatic hydrocarbon fuel in a diffusion flame to hydrogen and carbon radicals, and carbon-hydrogen radical fragments. These combine into larger aromatic layer plane units until they are no longer stable and condense out of the vapor phase to form nuclei, or growth centers. Further carbon deposition forms carbon particles that are the precursors of the nodules. The carbon particles collide and coalesce while undergoing further deposition of carbon layer planes and their surface, forming the nodules and aggregates with their characteristic onion microstructure as seen in the micrographs (25). The various steps in the sequence are not well understood. There is particular disagreement regarding the nucleation and particle formation steps preceding the formation of nodules. One suggestion is that the particles go through a fairly sticky stage as they collide and coalesce to form the aggregates. Another suggestion is that the layer planes formed in the vapor phase condense out to form solid multiple layer plane nuclei. Carbon deposition on the nuclei results in particles and eventually nodules and aggregates. The remarkable and industrially important influence of ionic species such as  $K^+$  and  $Ca^{2+}$  on the morphology of the aggregates and their surface area during the carbon black formation process is a strong indication that ionic mechanisms may be active in the nucleation and aggregate formation steps (22). There are several reviews of carbon formation mechanisms (26,27).

## Manufacture

### THE OIL-FURNACE PROCESS

The oil-furnace process, based on the partial combustion of liquid aromatic residual hydrocarbons, was first introduced in the United States at the end of World War II. It rapidly displaced the then dominant channel (impingement) and gas-furnace processes because it gave improved yields and better product qualities. It was also independent of the geographical source of raw materials, a limitation on the channel process and other processes dependent on natural gas, making possible the worldwide location of manufacturing closer to the tire customers. Environmentally it favored elimination of particulate air pollution and was more versatile than all other competing processes.

A simplified flow diagram of a modern furnace black production line is shown in Figure 7 (28). The principal pieces of equipment are the air blower, process air and oil preheaters, reactors, quench tower, bag filter, pelletizer, and rotary dryer. The basic process consists of atomizing the feedstock into the combustion zone of the reactor where the combustion of natural gas and preheated excess air create a high temperature environment of 1200 to 1900°C that almost instantly vaporizes the feedstock and decomposes most of it to carbon black and hydrogen. The remaining feedstock reacts with the excess oxygen in the primary combustion stream to maintain the reaction temperature for carbon formation. In some reactors a number of feedstock streams are atomized radially into the high velocity combustion gases. The reaction products must be quenched rapidly with water sprays to lower the temperature to prevent loss of the carbon black product through reaction with carbon dioxide and water, products of the combustion reactions. The hot, heavy carbon black smoke from the reactors enters the air preheater where thermal energy is transferred to preheat the primary combustion air. From the air preheater the lower temperature combustion products are given a secondary quench for a further lowering of temperature in a tower from which they enter the bag filter that separates the fluffy carbon black product from the tail gases. Since the tail gases are composed mainly of water, nitrogen, carbon monoxide, carbon dioxide, and hydrogen, they have heating value as a fuel to supplement the natural gas used to preheat feedstock and for heating the pellet dryers. Unused tail gas is frequently flared prior to venting to the atmosphere after removal of particulate matter. The fluffy carbon black from the bag filter is mechanically agitated to increase its bulk density and is then conveyed to the wet pelletizers where water is added to transform the product into wet granules. Dry pelletization in rotating drums is practiced for some special applications. The wet pellets are then dried in a rotary dryer after which finished product goes to storage tanks for shipping in bulk or in bags.

**Feedstocks.** Feedstocks are viscous aromatic hydrocarbons consisting of branched polynuclear aromatics with smaller quantities of paraffins and unsaturates. Preferred feedstocks are high in aromaticity, free of coke and other gritty materials, and contain low concentrations of asphaltene, sulfur, and alkali metals. Other limitations are the quantities available on a long-term basis, uniformity, ease of transportation, and cost. The ability to handle such oils in tanks, pumps, transfer lines, and spray nozzles are also primary requirements.

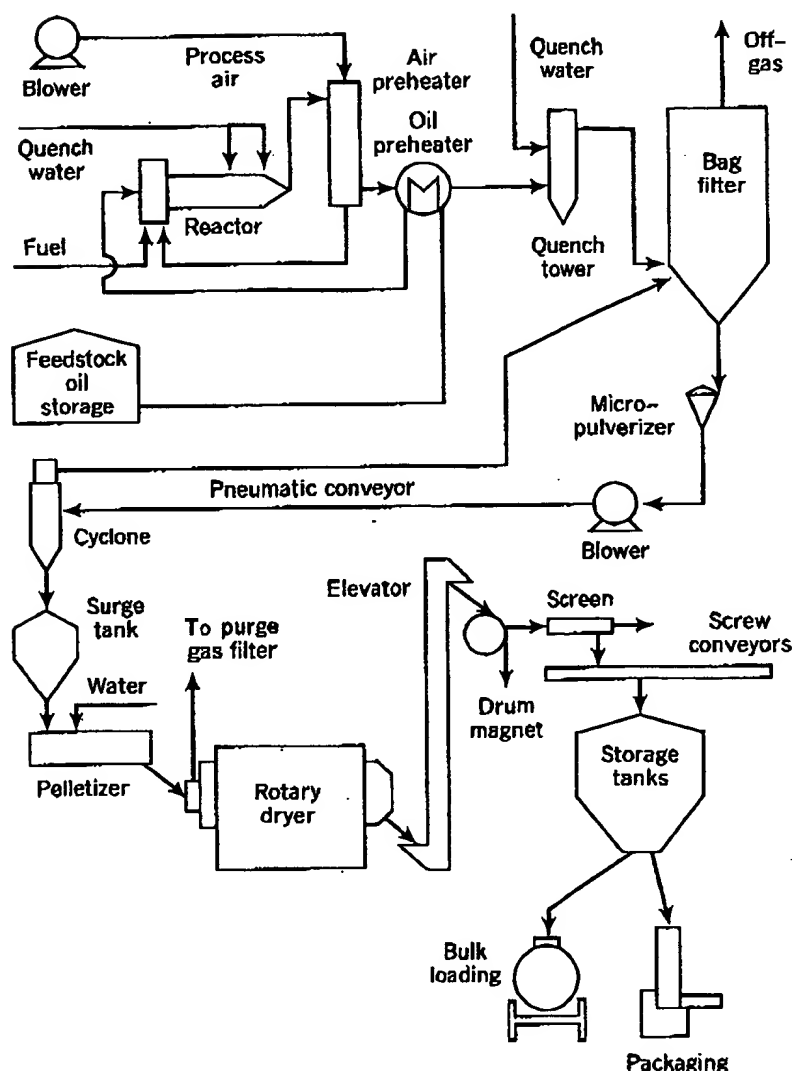


Fig. 7. Flow diagram of oil-furnace black process.

The principal sources of feedstocks in the United States are the decant oils from petroleum refining operations. These are clarified heavy distillates from the catalytic cracking of gas oils. About 95% of U.S. feedstock use is decant oil. Another source of feedstock is ethylene process tars obtained as the heavy by-products from the production of ethylene by steam cracking of alkanes, naphthas, and gas oils. There is a wide use of these feedstocks in European production. European and Asian operations also use significant quantities of coal tars, creosote oils, and anthracene oils, the distillates from the high temperature coking of coal. European feedstock sources are 50% decant oils and 50% ethylene tars and creosote oils.

Aromaticity is the most important property of a carbon black feedstock. It is generally measured by the Bureau of Mines Correlation Index (BMCI) and is an indication of the carbon-to-hydrogen ratio. The sulfur content is limited to reduce corrosion, loss of yield, and sulfur in the product. It may be limited in certain locations for environmental reasons. The boiling range must be low enough so that it will be completely volatilized under furnace time-temperature conditions.

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Alkane insolubles or asphaltenes must be kept below critical levels in order to maintain product quality. Excessive asphaltene content results in a loss of reinforcement and poor treadwear in tire applications.

The pricing of carbon black feedstocks depends on their alternate market as residual fuel oil, especially that of high sulfur No. 6 fuel oil. The actual price is determined by the supply/demand relationships for these two markets. Feedstock cost contributes about 60% of the total manufacturing cost. The market price of carbon black is strongly dependent on the feedstock cost as shown in Figure 8.

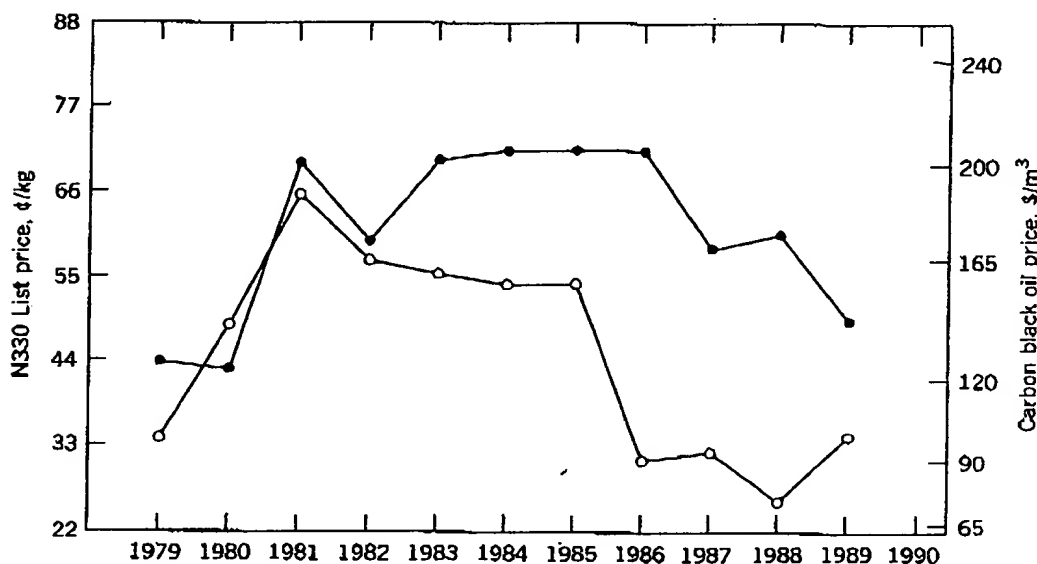


Fig. 8. Carbon black price and raw material cost in the United States (1979-1989). Average U.S. list price N330 (HAF)-grade carbon black,  $\text{\$/kg}$ . To convert  $\text{\$/m}^3$  to  $\text{\$/barrel}$ , multiply by 0.159.

**Reactors.** The heart of a furnace black plant is the furnace or reactor where carbon black formation takes place under high temperature, partial combustion conditions. The reactors are designed and constructed to be as trouble-free as possible over long periods of operation under extremely aggressive conditions. They are monitored constantly for signs of deterioration in order to ensure constant product quality. The wide variety of furnace black grades for rubber and pigment applications requires different reactor designs and sizes to cover the complete range, though closely related grades can be made in the same reactor by adjusting input variables. Reactors for higher surface area and reinforcing grades operate under high gas velocities, temperatures, and turbulence to ensure rapid mixing of reactant gases and feedstock. Lower surface area and less reinforcing grades are produced in larger reactors at lower temperatures, lower velocities, and longer residence time. Table 3 lists carbon formation temperatures, residence times, and maximum velocities for the complete surface area range of rubber-grade blacks. The N-series designation is in accordance with ASTM D1765, which is the standard classification system for carbon blacks used in rubber products (15). At least three different reactor designs must be used to make this range of furnace blacks and thermal black.

**Table 3. Time-Temperature-Velocity Conditions in Carbon Black Reactors<sup>a</sup>**

	Surface area, m <sup>2</sup> /g	Temperature, °C	Residence time, s	Maximum velocity, m/s
N100 series, SAF <sup>b</sup>	145	1800	0.008	
N200 series, ISAF <sup>b</sup>	120		0.010	180-400
N300 series, HAF <sup>c</sup>	80	1550	0.031	
N500 series, FEF <sup>d</sup>	42		1.0	30-80
N700 series, SRF <sup>e</sup>	25	1400	1.5	0.5-1.5
N990 thermal	8	1200-1350	10	10

<sup>a</sup>These characteristic conditions and values depend on reactor designs and fuel rates.

<sup>b</sup>SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace.

<sup>c</sup>HAF = high abrasion furnace.

<sup>d</sup>FEF = fast extrusion furnace.

<sup>e</sup>SRF = semireinforcing furnace.

Reactors are built to have three fairly well-defined zones. Gas and air are introduced into an upstream, primary combustion zone. For reinforcing grades, this connects with a mixing zone of high velocity and turbulence where feedstock is introduced as a fine atomized spray. The mixing zone is followed by a reaction zone of cylindrical shape where carbon-forming reactions occur. Downstream of the reaction zone is a water quench. For high surface area blacks the reactors may have a 15 to 38 cm diameter mixing zone with lengths up to five m. For lower area blacks the reactors are cylindrical with diameters of 75 cm or more and lengths of 9 to 12 m. There is a wide variety of reactors, and each manufacturer has proprietary designs. Air and gas may be introduced to the primary combustion zone either axially, tangentially, or radially. The feedstock can be introduced into the primary flame either axially or radially in the high velocity section of the mixing zone. The high velocity section may be venturi-shaped or consist of a narrow diameter choke. The reactors have a steel shell construction lined with high temperature-resistant castable refractories and insulating cements. The refractories have a service life of one to three years. Figures 9 and 10 show the designs of commercial reactors based on the patent literature.

The quality and yield of carbon black depends on the quality of the feedstock, reactor design, and input variables. The structure is controlled by the addition of alkali metals to the reaction or mixing zones. Usual practice is to use aqueous solutions of alkali metal salts such as potassium chloride or potassium hydroxide sprayed into the combustion chamber or added to the make oil in the oil injector. Alkaline-earth compounds such as calcium acetate that increase the specific surface area are introduced in a similar manner.

The energy utilization in the production of one kilogram of oil-furnace carbon black is in the range of  $9.3-16 \times 10^7$  J ( $4-6.9 \times 10^4$  Btu/lb), and the yields are 300-660 kg/m<sup>3</sup> (2.5-5.5 lb/gal) depending on the grade. The energy inputs to the reactor are the heat of combustion of the preheated feedstock, heat of combustion of natural gas, and the thermal energy of the preheated air. The energy output consists of the heat of combustion of the carbon black product, the heat of combustion and the sensible heat of the tail gas, the heat loss from the water

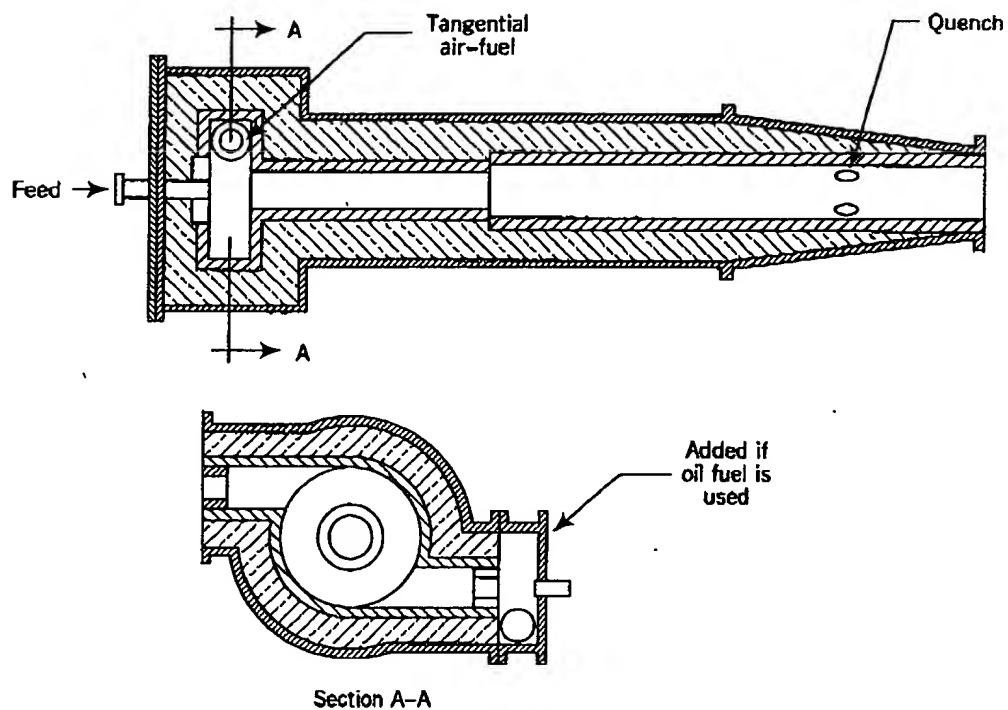


Fig. 9. Reactor for HAF-ISAF (N300-N200) carbon blacks. Courtesy of Phillips Petroleum Co.

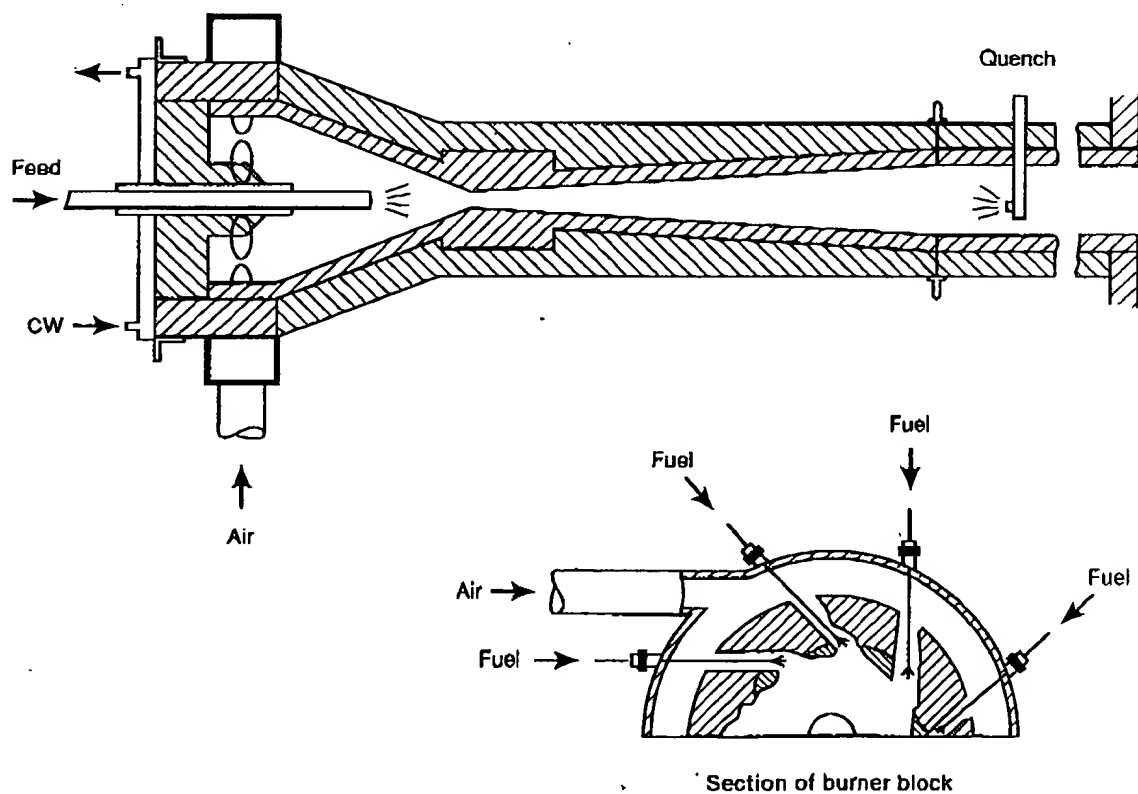


Fig. 10. Columbian reactor for tread blacks. CW = cold water.



quench, heat loss by radiation to atmosphere, and the heat transferred to preheat the primary combustion air. The energy balance for a N300 type of reinforcing grade is shown in Table 4. In this example the thermal efficiency of the process (without tail gas utilization) is 37% for a carbon yield of 0.63 kg/L (5 lb/gal), 61% based on feedstock.

**Table 4. Energy Balance for Reinforcing Grade of Carbon Black**

<i>Energy input</i>	
energy from feedstock (288°C preheat)	73%
energy from natural gas	23%
air preheat (400°C)	4%
<i>Energy output</i>	
carbon product (heat of combustion)	37%
tail gas (heat of combustion and sensible heat)	39%
heat loss from water quench	14%
heat loss to atmosphere	6%
air preheat (400°C)	4%

#### THERMAL BLACK PROCESS

Thermal black is a large particle size, low structure carbon black made by the thermal decomposition of natural gas, coke oven gas, or liquid hydrocarbons in the absence of air or flames. Its use in the United States in 1989 was estimated at about 54–68 million kg or about 4% of total consumption. Although at one time, based on cheap natural gas, thermal black was the least expensive of the regular rubber-grade blacks, it is today the most expensive. It is used in rubber and plastics applications for its unique properties of low hardness, high extensibility, low compression set, low hysteresis, and excellent processing. Its main uses are in O-rings and seals, hose, tire innerliners, V-belts, other mechanical goods, and in cross-linked polyethylene for electrical cables.

The thermal black process dates from 1922. The process is cyclic using two refractory-lined cylindrical furnaces or generators about 4 m in diameter and 10 m high. During operation, one generator is being heated with a near stoichiometric ratio of air and off-gas from the make generation whereas the other generator, heated to an average temperature of 1300°C, is fed with natural gas. The cycle between black production and heating is five minutes alternating between generators, resulting in a reasonably continuous flow of product and off-gases to downstream equipment. The effluent gas from the make cycle, which is about 90% hydrogen, carries the black to a quench tower where water sprays lower the temperature before entering the bag filter. The effluent gas is cooled and dehumidified in a water scrubber for use as fuel in the heating cycle. The collected black from the filters is conveyed to a magnetic separator, screened, and hammer-milled. It is then bagged or pelletized. The pelletized form is bagged or sent to bulk

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loading facilities. The yield is about 45% of the total carbon content of the process gas with an energy utilization of  $2 \times 10^8$  J/kg ( $0.85 \times 10^5$  Btu/lb).

**ACETYLENE BLACK PROCESS**

The high carbon content of acetylene (92%) and its property of decomposing exothermically to carbon and hydrogen make it an attractive raw material for conversion to carbon. Acetylene black is made by a continuous decomposition process at an atmospheric pressure of 800–1000°C in water-cooled metal retorts lined with refractory. The process consists in feeding acetylene into the hot reactors. The exothermic reaction is self-sustaining and requires water cooling to maintain a constant reaction temperature. The carbon black-laden hydrogen stream is then cooled followed by separation of the carbon from the hydrogen tail gas. The tail gas is either flared or used as fuel. After separation from the gas stream acetylene black is very fluffy with a bulk density of only 19 kg/m<sup>3</sup> (1.2 lb/ft<sup>3</sup>). It is difficult to compact and resists pelletization. Commercial grades are compressed to various bulk densities up to 200 kg/m<sup>3</sup> (12.5 lbs/ft<sup>3</sup>).

Acetylene black is very pure with a carbon content of 99.7%. It has a surface area of about 65 m<sup>2</sup>/g, an average particle diameter of 40 nm, and a very high but rather weak structure with a DBPA value of 250 mL/100 g. It is the most crystalline or graphitic of the commercial blacks. These unique features result in high electrical and thermal conductivity, low moisture absorption, and high liquid absorption.

A significant use of acetylene black is in dry cell batteries where it contributes low electrical resistance and high capacity. In rubber it gives electrically conductive properties to heater pads, tapes, antistatic belt drives, conveyor belts, and shoe soles. It is also useful in electrically conductive plastics such as electrical magnetic interference (EMI) shielding enclosures. Its contribution to thermal conductivity has been useful in rubber curing bags for tire manufacture. Production capacity for acetylene black in the United States in 1989 was 2.07 million kg from a single plant.

**LAMPBLACK PROCESS**

The lampblack process has the distinction of being the oldest and most primitive carbon black process still being practiced. The ancient Egyptians and Chinese employed techniques similar to modern methods collecting the lampblack by deposition on cool surfaces. Basically, the process consists of burning various liquid or molten raw materials in large, open, shallow pans 0.5 to 2 m in diameter and 16 cm deep under brick-lined flue enclosures with a restricted air supply. The smoke from the burning pans passes through low velocity settling chambers from which the carbon black is cleared by motor-driven ploughs. In more modern installations the black is separated by cyclones and filters. By varying the size of the burner pans and the amount of combustion air, the particle size and surface area can be controlled within narrow limits. Lampblacks have similar properties to the low area oil-furnace blacks. A typical lampblack has an average particle diameter of 65 nm, a surface area of 22 m<sup>2</sup>/g, and a DBPA of 130 mL/100 g. Production is small, mostly in Western and Eastern Europe. Its main use is in

paints, as a tinting pigment where blue tone is desired. In the rubber industry lampblack finds some special applications.

#### IMPINGEMENT (CHANNEL, ROLLER) PROCESS BLACKS

From World War I to World War II the channel black process made most of the carbon black used worldwide for rubber and pigment applications. The last channel black plant in the United States was closed in 1976. Operations still exist and are even being expanded in Europe. The demise of channel black was caused by environmental problems, cost, smoke pollution, and the rapid development of oil-furnace process grades that were equal or superior to channel black products particularly for use in synthetic rubber tires.

The name channel black came from the steel channel irons used to collect carbon black deposited by small natural gas flames impinging on their surface iron channels. Highly aromatic anthracene oils are used as raw material instead of natural gas. The black is scraped off the rollers, and the off-gases from the steel box enclosed rollers are passed through bag filters where additional black is collected. About half of the black is deposited on the rollers. The purified exhaust gases are vented to the atmosphere. The oils used in this process are high boiling and must be vaporized and conveyed to the large number of small burners by means of a combustible carrier gas. Yield of rubber-grade black is 60% and 10–30% for high quality color grades.

The characteristics of roller process impingement blacks are basically similar to those of channel blacks. They have an acidic pH, a volatile content of about 5%, surface area of about 100 m<sup>2</sup>/g, and an average particle diameter of 10–30 nm. The smaller particle size grades are used as color (pigment) blacks, and the 30-nm grade is used in rubber.

#### Characterization and Test Methods

Carbon blacks differ in particle or nodule size, surface area, aggregate size, and aggregate morphology. Surface activity is also a factor in performance, but this feature has been difficult to define or measure. The ultimate dispersible units are aggregates. Aggregate size distribution and morphology determine such properties as surface area, dibutyl phthalate absorption (DBPA), and testing strength. A complete review of the physicochemical characterization of carbon black has been published (21).

**Particle Size.** The electron microscope is the universally accepted instrument for measuring particle size, aggregate size, and aggregate morphology. Typical electron micrographs of rubber-grade carbon blacks are shown in Figure 11. The grades are classified according to the ASTM D1765 system (2). The first letter N represents a normal rate of cure in rubber, and the first digit represents the average particle size of the carbon black. The last two digits are arbitrarily assigned. Thus N330 is a normal curing grade with a particle diameter range of 26 to 30 nm.

Particle size measurements are made from a negative enlarged to 100,000 diameters (29). Automated image analyzers provide measurements of a variety of

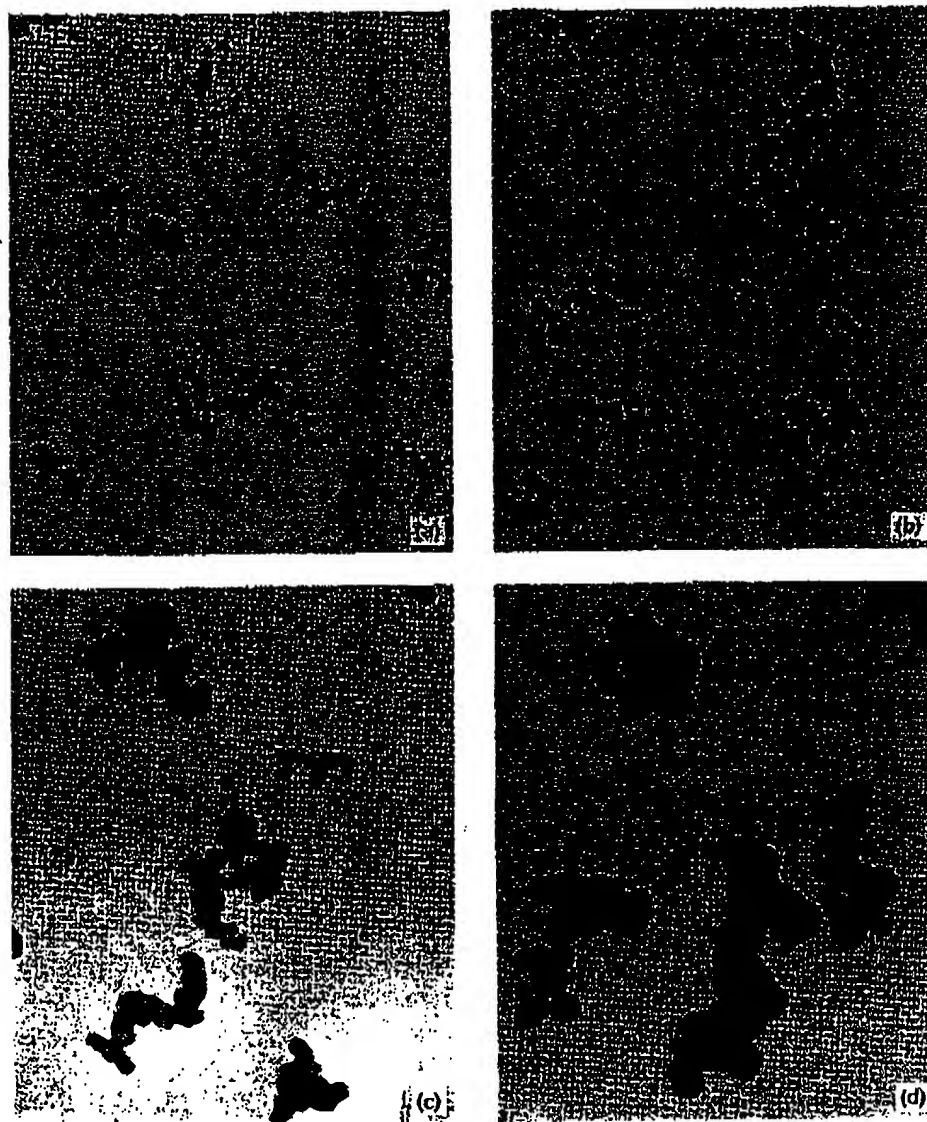


Fig. 11. Electron micrographs of rubber-grade carbon blacks where (a) is N110, (b) is N220, (c) is N550, and (d) is N762.

particle and aggregate parameters. Surface areas can be calculated from electron microscope measurements. These are in satisfactory agreement with surface areas determined by nitrogen adsorption measurements. Special pigment blacks and blacks used for electrical conductivity are highly porous, and the surface areas calculated from their particle diameters are very much smaller than those calculated from gas absorption.

**Surface Area.** The most important features influencing the performance of carbon blacks are aggregate size and surface area. Surface area is measured by gas- and liquid-phase adsorption techniques, and depends on the amount of adsorbate required to form a surface monolayer. If the area occupied by a single-adsorbate molecule is known, a simple calculation will yield the surface area. A low temperature nitrogen absorption method, based on the original method of

Brunauer, Emmett, and Teller (BET) (30), has been adopted by ASTM as standard method D3037-86 (2).

Liquid-phase adsorption methods are widely used for quality control and specification purposes. The adsorption of iodine from potassium iodide solution is the standard ASTM method D1510-83 (2). The surface area is expressed as the iodine number whose units are milligrams of iodine adsorbed per gram of carbon. It is quite fortuitous that the values of iodine numbers turn out to be about the same as the values for surface areas in square meters per gram by nitrogen adsorption for nonporous carbon blacks.

Another standard industry method for surface area is based on the adsorption of cetyltrimethylammonium bromide (CTAB) from aqueous solution. This is ASTM method D3765-85 (2). This method measures the specific surface area of carbon black exclusive of the internal area contained in micropores that are too small to admit the large CTAB molecules. For rubber-grade nonporous blacks the CTAB method gives excellent agreement with nitrogen surface areas.

**Structure and Aggregate Morphology.** Structure or aggregate morphology is another important characteristic that influences performance. Structure is determined by aggregate size and shape. These properties affect aggregate packing and the volume of voids in the bulk material. In liquid media structure affects rheological properties such as viscosity and yield point. In rubber, viscosity, extrusion die swell, modulus, and electrical conductivity are affected by structure. For classification and quality control purposes structure is assessed by measurements of void volume, either in the bulk by density or by the absorption of a liquid such as dibutyl phthalate (DBP). The dibutyl phthalate absorption number determination is ASTM method D2414-86 (2). The void volume in the bulk is usually measured under pressure. From the bulk density under a given pressure the volume of voids per unit weight of carbon is calculated.

**Tint Strength.** Tint strength is another industry method used for the classification of carbon blacks adopted by ASTM as D3265-85 (2). Tint strength is closely related to surface area and decreases with increasing aggregate size. It provides a rough estimate of the reinforcing potential of carbon black in rubber. In this test a small amount of carbon black is mixed with zinc oxide and an oil vehicle to produce a black or gray paste. The reflectance of this paste is measured and compared to the reflectance of a paste made with a reference black. The ratio of the reference black paste reflectance to the sample black multiplied by 100 is the tint strength.

There are many other test methods used to characterize carbon blacks for quality control and specification purposes. Table 5 lists some of these methods which, with a few exceptions, have been adopted by ASTM.

## Grades and Applications

U.S. consumption of carbon black in 1988 by various market sectors is shown in Table 6. About 90% of total consumption is in the rubber industry and 69% for tires. About 10% is consumed for other automotive products and 11% for rubber products unrelated to the automotive industry. The automotive industry accounts

**Table 5. Special Analytical Test Methods for Carbon Black**

Test method	Standard	Comment
iodine adsorption, mg/g	ASTM D1510	amount of iodine adsorbed from aqueous solution as a measure for the specific surface area; not applicable for oxidized or highly porous carbon blacks
N <sub>2</sub> surface area, m <sup>2</sup> /g	ASTM D3037	calculated from amount of adsorbed N <sub>2</sub> at liquid nitrogen temperature
CTAB surface area, m <sup>2</sup> /g	ASTM D3765	amount of cetyltrimethylammonium bromide adsorbed from aqueous solution as measure of specific nonporous (outer) surface area
aggregate dimension	ASTM D3849	determination of aggregate dimensions (unit length, width, etc) by electron microscope image analysis
aggregate size distribution		diameters of equivalent solid spheres that sediment at same rate as aggregates during centrifuging
DBP absorption, mL/100 g	ASTM D2414	determination of the void volume with dibutyl phthalate in a special kneader as measure of structure
void volume, mL/100 g		volume of voids from bulk density measurement under pressure
24M4-DBP absorption, mL/100 g	ASTM D3493	determination of DBP absorption after four repeated compressions at 165 MPa (24,000 psi)
jetness		light absorption of a carbon black paste in linseed oil; determination by visual comparison against standard blacks or by measuring the absolute light emission
tint strength, %	ASTM D3265	ability of a carbon black to darken a white pigment in a linseed oil paste; the tinting strength is the weight percentage of the standard carbon black with respect to the tested black to obtain the same gray tone; different standard white pigments and carbon black concentrations are used according to ASTM
volatiles, %	ASTM D1620	weight loss when calcined at 950°C for 7 min
heating loss (moisture), %	ASTM D1509	weight loss on drying at 125°C for 1 h
pH	ASTM D1512	pH of an aqueous slurry of carbon black; pH is mainly influenced by surface oxides
extractables, %	ASTM D3392	amount of material which can be extracted by a boiling solvent, usually toluene, in at least 8 h
		light absorption-transmission of a 1,2-dichlorobenzene solution of the extracted material

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Table 5. (Continued)

Test method	Standard	Comment
ash content, %	ASTM D1506	amount of noncombustible material after burning the carbon black at 675°C
sulfur content, %	ASTM D1619	
sieve residue, %	ASTM D1514	amount of coarse impurities that cannot be purged through a testing sieve by water
bulk density, g/L	ASTM D1513	measure for the densification of carbon black
tamped density, g/L		similar to bulk density; however, void volume is reduced by tamping
pellet size distribution	ASTM D1511	determination by means of sieve shaker
finest content, %	ASTM D1508	only for pelletized blacks; percentage passing through a sieve of 125 $\mu$ m (mesh) width

for 79% of consumption. Pigment applications account for about 10% of consumption, most of this for plastics and printing inks. Western Europe consumes 74% in tires and other automotive products and almost 20% in other industrial rubber products. Pigment applications in Western Europe and Japan are 5–6% of consumption.

Table 6. U.S. End Use Consumption of Carbon Black<sup>a</sup>

Market sector	Consumption, 10 <sup>3</sup> t	Percent of total, %
<i>Rubber</i>		
tires, treads, tubes	927	68.9
other automotive	132	9.8
molded, extruded, industrial products, roofing, etc	148	10.9
<i>Total rubber</i>	<i>1207</i>	<i>89.6</i>
<i>Nonrubber</i>		
plastics	59	4.4
printing inks	48	3.6
paint	9	0.7
paper	7	0.5
other	16	1.2
<i>Total nonrubber</i>	<i>139</i>	<i>10.4</i>

<sup>a</sup>1988.

**Rubber Goods.** A selected list of typical properties, taken from ASTM D1765 of rubber-grade carbon blacks (2), is shown in Table 7. In addition to the assigned ASTM N-numbers, the list includes the old letter designations, pour

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densities, structure (DBPA), surface areas, and tint data. The structure/area relationships of these grades, called the carbon black spectrum, is illustrated in Figure 12, which shows a diagram of DBPA values versus the nitrogen surface areas. Closely related grades are easily distinguished. A broad range of structure is available in the N700-N600 and N300 range of surface areas. Table 8 lists the principal rubber grades by their N-number classification, general rubber properties, and typical uses. The behavior of different grades is dominated mainly by surface area and structure (DBPA). High surface area produces high reinforcement as reflected in high tensile and tear strengths, high resistance to abrasive wear, higher hysteresis, and poorer dynamic performance. A present day challenge to carbon black technologists is to optimize the balance between tire wear and tire hysteresis or the rolling resistance. Some progress on this problem has been made by using new furnace designs and other process variables that broaden the aggregate size distributions and lower the tint strength while maintaining surface area, structure, and reinforcement (31,32).

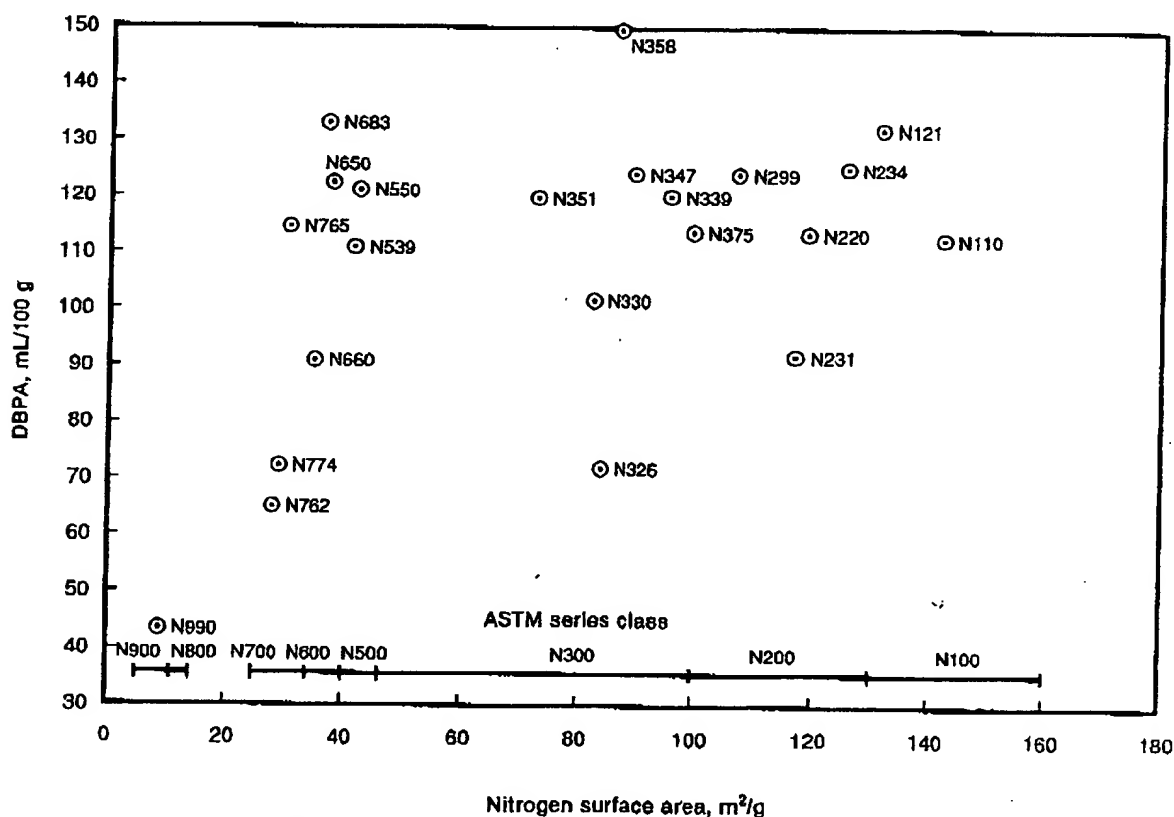


Fig. 12. Rubber grades carbon black spectrum.

The consumption of the various carbon black grades can be divided into tread grades for tire reinforcement and nontread grades for nontread tire use and other rubber applications. Table 9 shows the distribution of production of types for these uses. In the United States 55% production is for tread grades. In Western Europe tread-grade production is 64%, and in Japan it is 60%.



Table 7. Typical Properties Rubber-Grade Carbon Blacks<sup>a</sup>

ASTM designation	Former industry designation <sup>b</sup>	I <sub>2</sub> absorption number (D1510), g/kg	DBPA <sup>c</sup> (D2414), mL/100 g	DBPA <sup>c</sup> (compressed sample) (D3493), mL/100 g	CTAB <sup>d</sup> surface area (D3766), m <sup>2</sup> /g	Nitrogen surface area (D3087), m <sup>2</sup> /g	Tinting strength (D3286)	Pour density (D1513), kg/m <sup>3</sup>
N110	SAF	145	112	98	126	143	124	335
N121	SAF-HS	121	132	112	121	132	121	320
N220	ISAF	121	114	100	111	119	115	345
N231	ISAF-LM	121	92	86	108	117	117	390
N234	ISAF-HS	120	125	100	119	126	124	320
N239	ISAF-HS	108	124	105	104	108	113	335
N326	HAF-LS	82	72	69	83	84	112	465
N330	HAF	82	102	88	83	83	103	275
N339	HAF-HS	90	120	101	95	96	110	345
N347	HAF-HS	90	124	100	88	90	103	335
N351	HAF-HS	68	120	97	74	73	100	345
N358	HAF-HS	84	150	112	88	87	99	290
N375	HAF-HS	90	114	97	99	100	115	345
N539	FEF	43	111	84	41	41	0	385
N550	FEF	43	121	88	42	42	0	360
N650	GPF-HS	36	122	87	38	38	0	370
N660	GPF	36	90	75	35	35	0	425
N693	GPF-HS	35	133	0	39	37	0	335
N762	SRF	27	65	57	29	28	0	505
N765	SRF-HS	31	115	86	33	31	0	375
N774	SRF	29	72	62	29	29	0	495
N990	MT	0	43	40	9	9	0	0

<sup>a</sup>ASTM D1765.<sup>b</sup>SAF = super abrasion furnace; ISAF = intermediate super abrasion furnace; HAF = high abrasion furnace; FEF = fast extrusion furnace; GPF = general purpose furnace; SRF = semireinforcing furnace; MT = medium thermal; HS = high structure; LS = low structure; LM = low modulus.<sup>c</sup>Dibutyl phthalate [84-74-2] absorption.<sup>d</sup>Cetyl trimethylammonium bromide [57-09-0].

**Table 8. Applications of Principal Rubber-Grade Carbon Blacks**

Designation	General rubber properties	Typical uses
N110, N121	high abrasion resistance	special tire treads, airplane, off-the-road racing
N220, N299, N234	high abrasion resistance, good processing	passenger, off-the-road, special service tire treads
N339, N347, N375, N330	high abrasion resistance, easy processing, good abrasion resistance	standard tire treads, rail pads, solid wheels, mats, tire belt, sidewall, carcass retread compounds
N326	low modulus, good tear strength, good fatigue, good flex cracking resistance	tire belt, carcass, sidewall compounds, bushings, weather strips, hoses
N550	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, sidewall, innertubes, hose, extruded goods, v-belts
N650	high modulus, high hardness, low die swell, smooth extrusion	tire innerliners, carcass, belt, sidewall compounds, seals, friction compounds, sheeting
N660	high modulus, high hardness, low die swell, smooth extrusion	carcass, sidewall, bead compounds, innerliners, seals, cable jackets, hose, soling, EPDM compounds
N762	high elongation and resilience, low compression set	mechanical goods, footwear, innertubes, innerliners, mats

**Table 9. Carbon Black Production<sup>a</sup> by Grade, 10<sup>3</sup> t**

	United States	Western Europe	Japan
N100	35	28	37.1
N200	158	161	118
N300	555	528	300
<i>Total tread grades</i>	748	717	418
percent	55.2	63.8	59.5
N500	120	153	136
N600	326	137	87
N700	129	103	29
N900 (thermal)	23		9
<i>Total nontread grades</i>	598	393	261
percent	44.1	35.0	37.1
other grades			
acetylene	9.1	14	24
<i>Total carbon black</i>	1355	1124	703

<sup>a</sup>1998.

**Special-Grade Carbon Blacks.** In 1988 over 10% of U.S. consumption of carbon black was for nonrubber applications, ie, special blacks. In Europe and Japan about 5% is consumed for these uses. Most of the special black grades are manufactured by methods to meet specific product specifications required for their end uses. They sell for a higher average price than the rubber grades. These markets have been growing at an average annual rate twice that of the rubber black grades. Of increasing importance in recent years have been applications in plastics to improve weathering resistance and to impart antistatic and electrically conductive properties.

About 42% of special blacks are used in plastics, 35% in printing inks, 7% in paper, and 16% in miscellaneous applications. News inks account for most of the printing ink market. Electrical applications have been taking an increasing share of the plastics market. Medium and high color grades, in their normal and surface-oxidized versions, are used in enamels, lacquers, and plastics for their extreme jetness. Typical properties of special grades of furnace blacks are listed in Table 10. The list is divided into normal furnace grades and surface oxidized grades. Increased surface oxidation decreases viscosity, improves dispersion, and increases the flow behavior in many liquid systems. The volatile content is an indication of the degree of surface oxidation. To improve dispersion and flow, special blacks generally are produced at lower structural (DBPA) and bulk density values than rubber-grade carbon blacks.

Table 11 lists the types and applications of special pigment-grade carbon blacks. Included in this list are thermal black and lampblack. Over 40 special black grades have been developed based on the furnace process having a broad range of surface areas, from 20 m<sup>2</sup>/g to over 1500 m<sup>2</sup>/g. The lower surface area products are used in printing inks and tinting. The high area, more expensive products find use in high color enamels and lacquers.

**Electrically Conductive Grades.** An important application of carbon black is to produce electrically conductive and antistatic polymer composites. These applications include antistatic carpet backing and floor tile, electrical heating elements, high voltage cable semiconductive shields, video tapes and disks, and EMI shielding. The electrical conductivity of bulk carbon black under compression is in the range of 0.02 to 0.5 ohm-cm. The conductivity of conductive carbon black-filled rubber and plastics is in the range of 1 to 10<sup>8</sup> ohm-cm. There is no clear relationship between bulk black conductivity and compound conductivity. The main variable determining compound conductivity is the carbon black concentration. At high enough concentrations all carbon blacks can produce compound resistivities of about 1.0 ohm-cm. For superconductive carbon black this concentration is 7–8% and for thermal black the required concentration is 65–70%. Figure 13 shows the concentration/resistivity relationships of selected carbon blacks covering the complete range of rubber and conductive grades (33). It can be seen that there is a critical concentration for each grade of carbon black above which the resistivity drops precipitously. This is often referred to as the percolation concentration.

The main carbon black characteristics determining its conductive behavior are surface area, aggregate morphology, and degree of graphitization or crystallinity. The high conductivity of acetylene black is attributed to its highly developed structure and its crystallinity. High conductivity furnace-grade blacks have

**Table 10. Furnace Process Special Grades for Pigment Applications in Inks, Plastics, Paints, and Paper**

Industry classification	N <sub>2</sub> surface area, m <sup>2</sup> /g	Particle diameter, nm	DBPA <sup>a</sup> , mL/100 g		Bulk density, g/L		Nigrometer <sup>b</sup> index	Tinting strength	Volatile, %	pH
			Fluffy	Pellets	Fluffy	Pellets				
high color	250-300	14-15	70-75	60-65	50-300	400-550	65-76	117-124	1.2-2.0	7-10
medium color	150-220	16-24	47-122	46-117	130-300	390-550	74-78	118-124	1.0-1.5	8-10
regular color	45-140	20-37	42-125	42-124	176-420	350-600	84-93	73-119	0.9-1.5	6-10
low color	25-45	41-75	71	64-120	256	352-512	94-99	48-69	0.6-0.9	8-10
<i>Surface oxidized grades</i>										
high color	400-600	10-20	121	105			64	100-135	8.0-9.5	2.0-3.3
medium color (long flow)	100-38	23-24	49-60	55	240-360	530	83-84	112-135	3.5-5.0	2.5-4.0
medium color (medium flow)	96-110	25	49-72	70	225-360	480	84	112-114	2.5-3.5	4.0-4.5
low color	30-40	50-56	48-93		260-500		92-100	64	3.5	3.0

<sup>a</sup>Dibutyl phthalate absorption.<sup>b</sup>A method for measuring the diffuse reflectance from a black paste with a black tile standard. The low numbers represent the jettest or most intense black grades.

**Table 11. Types and Applications of Special Pigment Grades of Carbon Blacks**

Type	Surface area, m <sup>2</sup> /g	DBPA <sup>a</sup> , mL/100 g	Volatile content, %	Uses
<i>Normal grades</i>				
high color	230-560	50-120	2	high jetness for alkyl and acrylic enamels, lacquers, and plastics
medium color	220-220	70-120	1-1.5	medium jetness and good dispersion for paints and plastics; ultraviolet and weathering protection for plastics
regular color	80-140	60-114	1-1.5	for general pigment applications in inks, paints, plastics, and paper; gives ultraviolet protection in plastics, high tint, jetness, gloss, and dispersibility in inks and paints
	46	60	1.0	good tinting strength, blue tone, low viscosity; used in gravure and carbon paper inks, paints, and plastics
	45-85	73-100	1.0	main use is in inks; standard and offset news inks
low color	25-42	64-120	1.0	excellent tinting black-blue tone; used for inks-gravure, one-time carbon paper inks; also for paints, sealants, plastics, and cements
thermal blacks	7-15	30-35	<0.5	tinting-blue tone; plastics and utility paints
lamp blacks	20-95	100-160	0.4-0.9	paints for tinting-blue tone
<i>Surface oxidized grades</i>				
high color	400-600	105-121	8.0-9.5	used for maximum jetness in lacquers, coatings, plastics, fibers, record disks
medium color, long flow	138	55-60	5	used in lithographic, letterpress, carbon paper, and typewriter ribbon inks; high jetness, excellent flow, low viscosity, high tinting strength, gloss, and good dispersability
medium color, long flow	96	70	2.5	used for gloss printing and carbon paper inks; excellent jetness, dispersibility; tinting strength, and gloss in paints
low color	30-40	48-93	3.5	used for tinting where flooding is a problem; easy dispersion

<sup>a</sup>Dibutyl phthalate absorption.

## 1066 CARBON (CARBON BLACK)

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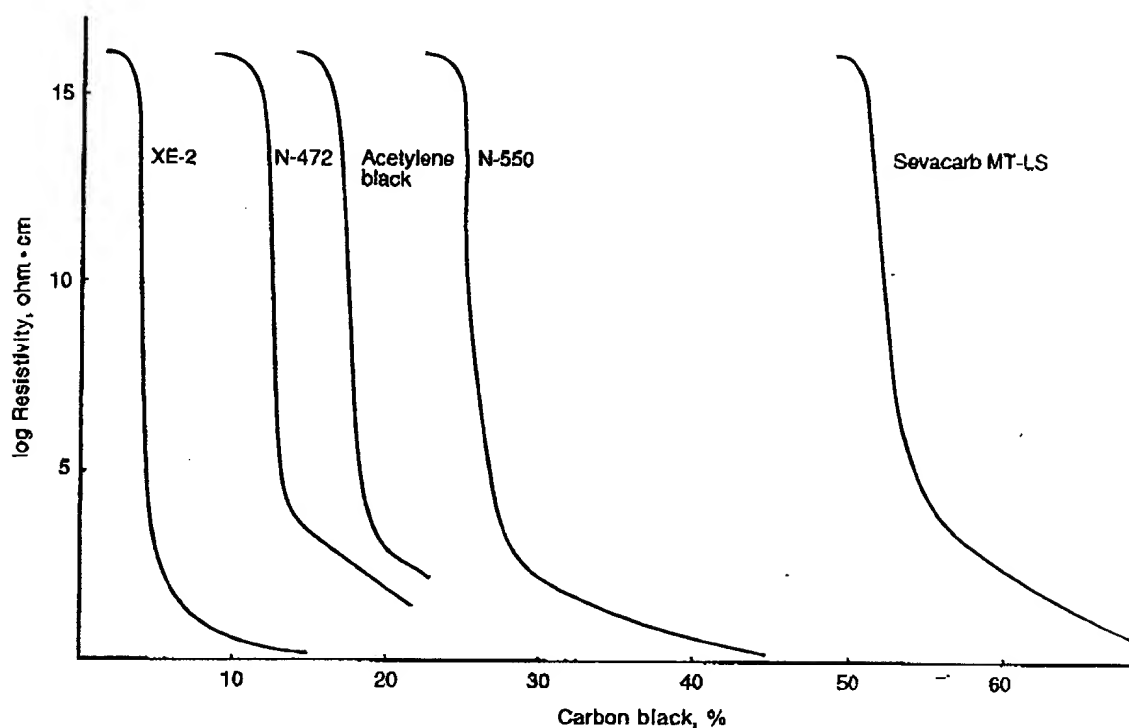


Fig. 13. Electrical resistivity versus carbon black concentration.

very high surface areas and structures (DBPA). Superconductive blacks, by-products of synthesis gas manufacture, have very high surface areas, highly developed structures, and a high degree of crystallinity.

The effect of surface area on conductivity was shown for channel-grade blacks in 1949 (34) and the surface area relationship to conductivity for furnace blacks in 1954 (35). High surface area is associated with increasing surface roughness and internal porosity rather than decreased particle or nodule size. Because of the decreased density of the aggregates resulting from the porosity of high surface area conductive blacks, they possess a larger number of aggregates per unit weight. At a given weight concentration, closer packing of aggregates increases conductivity. Crystallinity increases with high porosity contributing to high conductivity. The crystallinity increase results from the burnout of the more amorphous regions of the aggregate during manufacture.

The mechanism of electrical conduction in composites occurs by a process of electron tunneling through the polymer phase (36). Electrons tunnel from the black aggregates to their nearest neighbor. The resistivity of vulcanizates is a function of the average distance between aggregates (37). In addition to carbon black concentration, this gap distance depends on particle size, surface area, and aggregate morphology.

There are a number of publications on the properties and applications of electrically conductive carbon blacks (38-40). Figure 14 shows the electron micrographs of two grades of electrically conductive carbon blacks. The furnace blacks have the particle size of N200-N300 types. Their high surface areas indicate high internal porosity. Table 12 shows typical data and uses for eight electrically

conductive grades of carbon black and by-product carbons. The large differences between the nitrogen surface areas and the areas measured by cetyltrimethylammonium bromide (CTAB) absorption are because of internal porosity. The CTAB molecules are so large that they do not penetrate the pores available to the nitrogen molecules. The large, bulky aggregates, the high porosities, and low aggregate densities of the electrical grades produce high DBPA values, much larger than for normal furnace blacks.

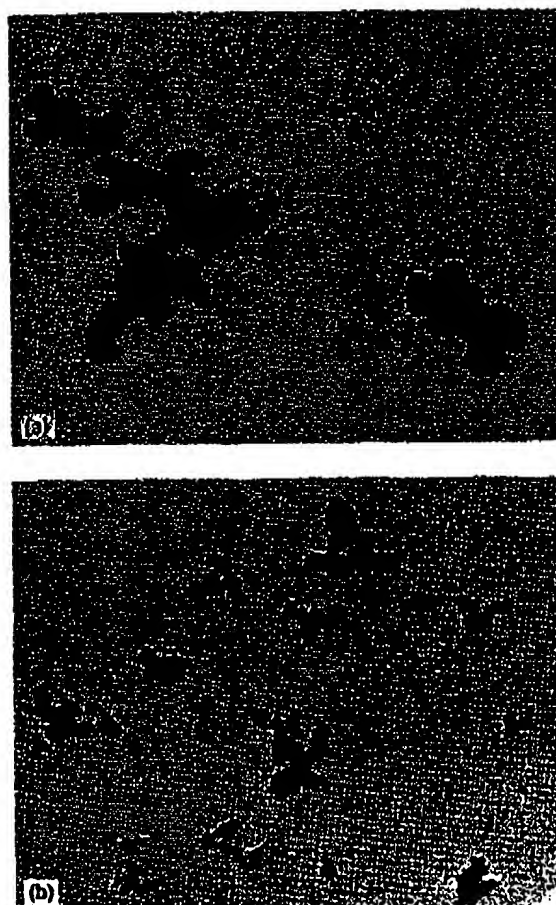


Fig. 14. Electron micrographs of electrically conductive grades of carbon black where (a) is Vulcan XC-72 (Cabot) (100,000  $\times$ ) and (b) is Vulcan P (Cabot) (100,000  $\times$ ).

### Carbon Black Manufacture and Market

**Manufacturers and Productions.** The consumption of carbon black in the United States reached a peak of 1,506,000 t during the beginning of the oil crisis in 1973. Then consumption decreased to 1,210,000 t in 1989. A number of events have contributed to decreased consumption by the rubber and tire industries including tire radialization, increased tire mileage, downsizing of tires, and increased imports of foreign cars. The negative influence of these events have pretty much run their course, and during the last 10 years there has been a modest growth in

**Table 12. Typical Data and Uses for Electrically Conductive Grades of Carbon Blacks**

Type	Particle diameter, nm	N <sub>2</sub> Surface area, m <sup>2</sup> /g	CTAB Surface area, m <sup>2</sup> /g	DBPA <sup>a</sup> mL/100 g	Tinting strength, D3265	Uses
acetylene black	42	64		300	52	high voltage semiconductive shields, conductive rubber, and plastics
conductive furnace (CF)N293	22	145	114	100	117	conductive rubber and plastics, carpet backing
conductive furnace (CF)N742	22	270	145	178	82	conductive and antistatic rubber and plastics products
superconductive furnace (SCF)		1475		330	163	electromagnetic interference shielding (EMI) compounds, videodisks, tapes, etc
synthesis gas by-product carbon	30	1000		245	124	EMI, videodisks, PTC <sup>b</sup> compounds (for heating tapes)
		800		365		
		1000	620	400		
		1250		495		

<sup>a</sup>Dibutyl phthalate absorption.<sup>b</sup>PTC = positive temperature coefficient.



carbon black production. Production for the period 1973–1989 is shown in Figure 15.

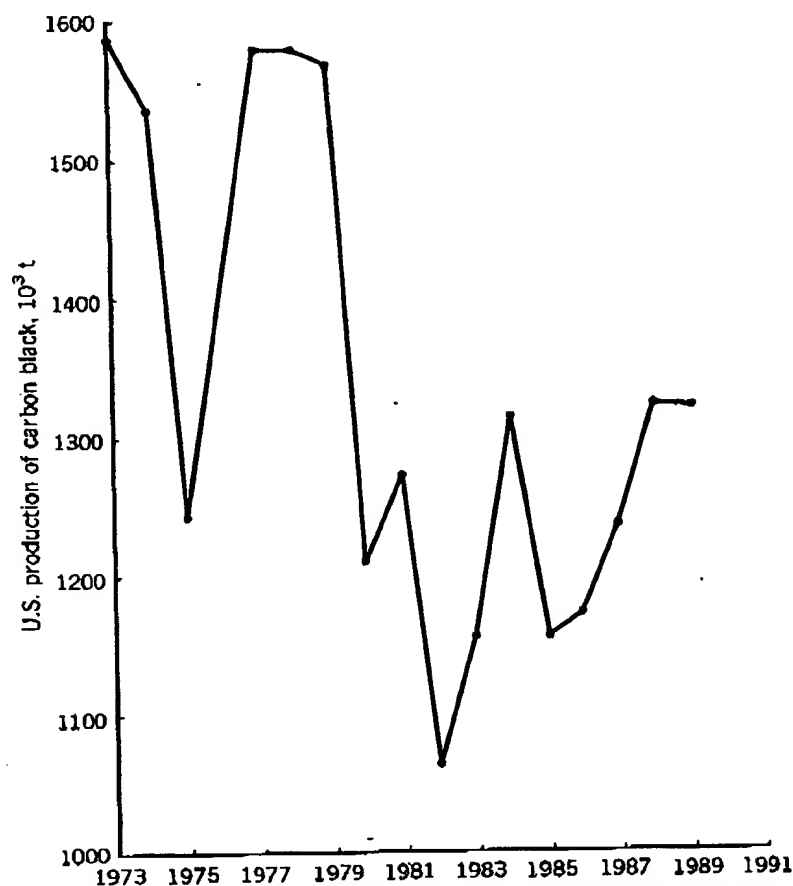


Fig. 15. U.S. production of carbon black (1973–1989).

The shrinkage in demand has resulted in a restructuring of the carbon black industry. Several of the principal multinational oil companies have left the business including Ashland, Cities Service Co., Phillips, and Conoco. Some plants have changed ownership. In the United States this has increased the production capacities of Degussa, Sid Richardson, and Huber. Today's U.S. industry consists of six principal producers. Rated capacities of the six U.S. manufacturers is shown in Table 13. Cabot Corp. and Columbian Chemicals are the leading producers, followed by Degussa, Sid Richardson, J. M. Huber Corp., and Witco. A survey of the future markets and present structure of the carbon black industry has been presented (1).

World carbon black rated capacities are shown in Table 14. North America has the largest capacity. Europe, Southeast Asia, and Russia/Eastern Europe have about equal capacities and Africa and the Middle East have only small production. The growth areas are predicted to be Southeast Asia and the Russia/Eastern Europe markets. The capacities for certain areas such as China and Russia/Eastern Europe should be taken as rough estimates.

**Table 13. U.S. Carbon Black Manufacturers Nameplate Capacities, 1988**

Manufacturers	Capacity 10 <sup>3</sup> t	U.S. capacity, %
Cabot Corp.		
Franklin, La.	153	
Pampa, Tex.	32	
Parkersburg, W.Va.	83	
Ville Platte, La.	126	
<i>Total</i>	<i>394</i>	25
Columbian Chemicals		
El Dorado, Ark.	75	
North Bend, La.	121	
Hickok, Kans.	38	
Moundsville, W.Va.	82	
<i>Total</i>	<i>316</i>	20
Degussa		
Arkansas Pass, Tex.	82	
Ivanhoe, La.	100	
Belpre, Ohio	55	
<i>Total</i>	<i>237</i>	15
Sid Richardson Co.		
Addis, La.	62	
Big Spring, Tex.	57	
Borger, Tex.	125	
<i>Total</i>	<i>244</i>	15.5
J. M. Huber Corp.		
Orange, Tex.	62	
Baytown, Tex.	102	
Borger, Tex.—Furnace	57	
Thermal	23	
<i>Total</i>	<i>244</i>	15.5
Witco Corp.		
Phenix City, Ala.	25	
Ponca City, Okla.	68	
Sunray, Tex.	46	
<i>Total</i>	<i>139</i>	8.8
<i>Total U.S. capacity</i>	<i>1574</i>	

**Product Safety**

The safety aspects of carbon black have been the subject of a number of reviews and articles (41–43). The manufacture of carbon results in trace amounts of organic and inorganic impurities. These impurities have been suspected of causing potential health problems. Of particular concern have been the salts of toxic metals and adsorbed polynuclear aromatic hydrocarbons (PNAs). A few of the polyaromatic hydrocarbons are known to be mutagens and/or animal carcinogens. The solvent extract of furnace blacks is in the range of 300 to 2000 ppm (0.03–0.20%). Most of this extract consists of 10–15 organic compounds, the

**Table 14. World Carbon Black Capacities by Region and Country, 1988**

Region	Number of plants	Estimated capacity, 10 <sup>3</sup> t
<b>North America</b>		
United States	22 <sup>a</sup>	1565 <sup>a</sup>
Canada	3 <sup>a</sup>	182
Mexico	2	158
<i>Total</i>	<i>27</i>	<i>1095</i>
<b>South America</b>		
Argentina	1	48
Brazil	3	199
Colombia	2	36
Peru	1	8
Venezuela	1	40
<i>Total</i>	<i>8</i>	<i>331</i>
<b>Europe</b>		
Great Britain	2	140
France	3	239
Germany	5	385
The Netherlands	2	120
Italy	3	191
Portugal	1	21
Spain	3	104
Sweden	1	33
<i>Total</i>	<i>20</i>	<i>1233</i>
<b>Australia/South East Asia</b>		
Australia	2	76
India	7	153
China <sup>b</sup>	30-45	500
Japan	12	766
South Korea	3	170
Malaysia	1	23
Pakistan	1	10
Philippines	1	15
Taiwan	1	53
Thailand	1	20
<i>Total</i>	<i>32</i>	<i>1786</i>
<b>Africa</b>	<i>2</i>	<i>75</i>
<b>Middle East</b>		
Iran	1	15
Turkey	1	35
<i>Total</i>	<i>2</i>	<i>50</i>
<b>Russia/Eastern Europe</b>		
Russia <sup>b</sup>	14	1300
Yugoslavia	1	36
Poland		58
Romania		130
Czechoslovakia		64
<i>Total</i>		<i>1588</i>
<i>Total world capacity</i>		<i>6968</i>

<sup>a</sup>Includes one thermal black plant (capacity, 25,000 t).<sup>b</sup>Estimate.

majority of which are not genotoxic. One compound that is toxic is benzo [ $\alpha$ ] pyrene [50-32-8], B $\alpha$ P, often used as an indicator of potential hazard. B $\alpha$ P ranges from 0 to 50 ppm and is less than one percent of the total extract. There have been a number of studies initiated by the U.S. carbon black industry to examine the health effects of various commercial carbon blacks and their benzene extracts. Tests have been made using laboratory animals. Investigations on absorption and elution effects in stomach fluids and human blood have been conducted. Although the solvent extracts of carbon black do show toxic properties, the aqueous systems of concern in humans show no elution of B $\alpha$ P and no toxic properties. The B $\alpha$ P is believed to be so strongly absorbed on the surface of carbon black and in such high dilution that it is inactive in animal testing for carcinogenicity. Statistical studies on the frequency of cancer of long-term employees in a carbon black plant covering a period of 17 years (1939-1956) has been reported (44). There is no evidence of increased cancer risk from exposure to industrial carbon blacks. The scientific literature based on animal research as well as observations on carbon black plant employees show no evidence of detrimental health effects. Most studies of carbon black dust inhalation and intratracheal administration with animals indicate that carbon black is not carcinogenic. OSHA regulations for carbon black dust concentrations call for an average exposure level over a given time period of not more than 3.5 mg/m<sup>3</sup>.

### Environmental Aspects

The carbon black industry takes extreme efforts to confine product during all stages of manufacture (45). Highly efficient bag filters are used to collect the product. After collection the fluffy carbon black is densified and pelletized to minimize dusting problems during shipping and use.

The process gases from the filters consist of nitrogen, carbon monoxide, carbon dioxide, hydrogen, water, small amounts of hydrogen sulfide, and other sulfur- and nitrogen-containing gases. In the past the process gases have been flared. Process gas is used as a fuel for in-plant heat needs, and where local conditions warrant, it may be burned to generate steam or power.

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**DIAMOND, NATURAL**

Naturally occurring diamond is a relatively rare polymorphic form of carbon characterized by a three-dimensional arrangement of tetrahedrally coordinated carbon atoms. Both natural and synthesized diamond [7782-40-3] have the highest hardness of all known materials, the highest thermal conductivity at room temperature, a high refractive index and optical dispersion, a low thermal expansion, and a relatively high inertness to chemical attack. This unique combination of properties permits diamond to be foremost in certain applications: as a highly prized gemstone; industrially as an important abrasive material unsurpassed in certain cutting, drilling, sawing, machining, grinding, and polishing operations for many materials; and in electronic and optical applications as a heat sink and window material, respectively.

**Occurrence and Exploration**

Diamonds were first discovered in ancient times in India and Borneo and later in Brazil in 1670 in alluvial deposits where water had sorted minerals on the basis of density and toughness. This type of tumbling often concentrates the better quality crystals such as those found in the ocean off the west coast of Africa. Exploration can be done by stream panning or drilling in conjunction with a search for the heavy mineral assemblages that accompany diamond. Alluvial deposits account for about 40% of the diamond found in primary sources.

Upstream exploration has sometimes led to the discovery of the primary source of alluvial stones, namely, kimberlite "pipes." These structures of igneous origin are the principal source of natural diamonds, and there are over 1000 occurrences of them in the world. Only a small number contain a high enough concentration of diamonds to warrant mining. Even in successful mining operations the ratio of diamond to the gangue that has to be removed and crushed is of the order of one part in a million or even less, of which the proportion of gem

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## CLAYS

Survey, 381

Uses, 405

### SURVEY

The terms clay or clays commonly refer to either rocks that may be consolidated or unconsolidated, or a group of minerals having unique properties. Traditionally, clays (rocks) are distinctive in at least two properties which render them technologically useful: plasticity and composition. Plasticity signifies the property of the clay when wetted that permits deformation by application of relatively slight pressure and retention of the deformed shape after release of the pressure. This property distinguishes clay from hard rocks. Clays are predominantly composed of hydrous phyllosilicates, referred to as clay minerals. These are hydrous silicates of Al, Mg, K, and Fe, and other less abundant elements. Clay minerals are extremely fine crystals or particles, often colloidal in size and usually platelike in shape. The nonclay mineral portion of clays (rocks) may consist of other minerals, portions of rocks, and organic compounds.

The very fine particles yield very large specific surface areas that are physically sorptive and chemically surface reactive. Many clay mineral crystals carry an excess negative electric charge owing to internal substitution by lower valent cations, and thereby increase internal reactivity in chemical combination and ion exchange. Clays, which may have served as substrates selectively absorbing and catalyzing amino acids in the origin of life, apparently catalyze petroleum formation in rocks (see PETROLEUM).

Because clays (rocks) usually contain more than one mineral and the various clay minerals differ in chemical and physical properties, the term clay may signify entirely different things to different clay users. Whereas the geologist views clay as a raw material for shale, the pedologist as a dynamic system to support plant life, and the ceramist as a body to be processed in preparation for vitrification, the chemist and technologist view clay as a catalyst, adsorbent, filler, coater, or source of aluminum or lithium compounds, etc.

For geologists, clay refers to sediments or sedimentary rock particles having a diameter of 3.9  $\mu\text{m}$  or less. Soil scientists define clays as disperse systems of the colloidal products of weathering in which secondary mineral particles of dimensions smaller than 2  $\mu\text{m}$  predominate. Ceramists, who probably process the greatest quantity of clay, usually emphasize aluminosilicate content and plasticity (1). Plasticity is defined as resulting from colloids of organic or mineral nature (2) but it may also arise from other causes (3). Even the origin of the clay has been included in one definition (4). Clay has been recognized as being a product of deep-seated alteration of silicate minerals by hydrothermal solutions rising from an igneous source as well as a product of surface weathering (5,6). Although clay minerals are usually considered breakdown products of silicates, largely by hydrolysis, clays may be built up from hydrates of silica and alumina (7).

A clay deposit usually contains nonclaylike minerals as impurities and these impurities may actually be essential in determining the unique and specially de-



sired properties of the clay. Both crystalline and amorphous minerals and compounds may be present in a clay deposit (8).

A broad definition of clays includes the following properties:

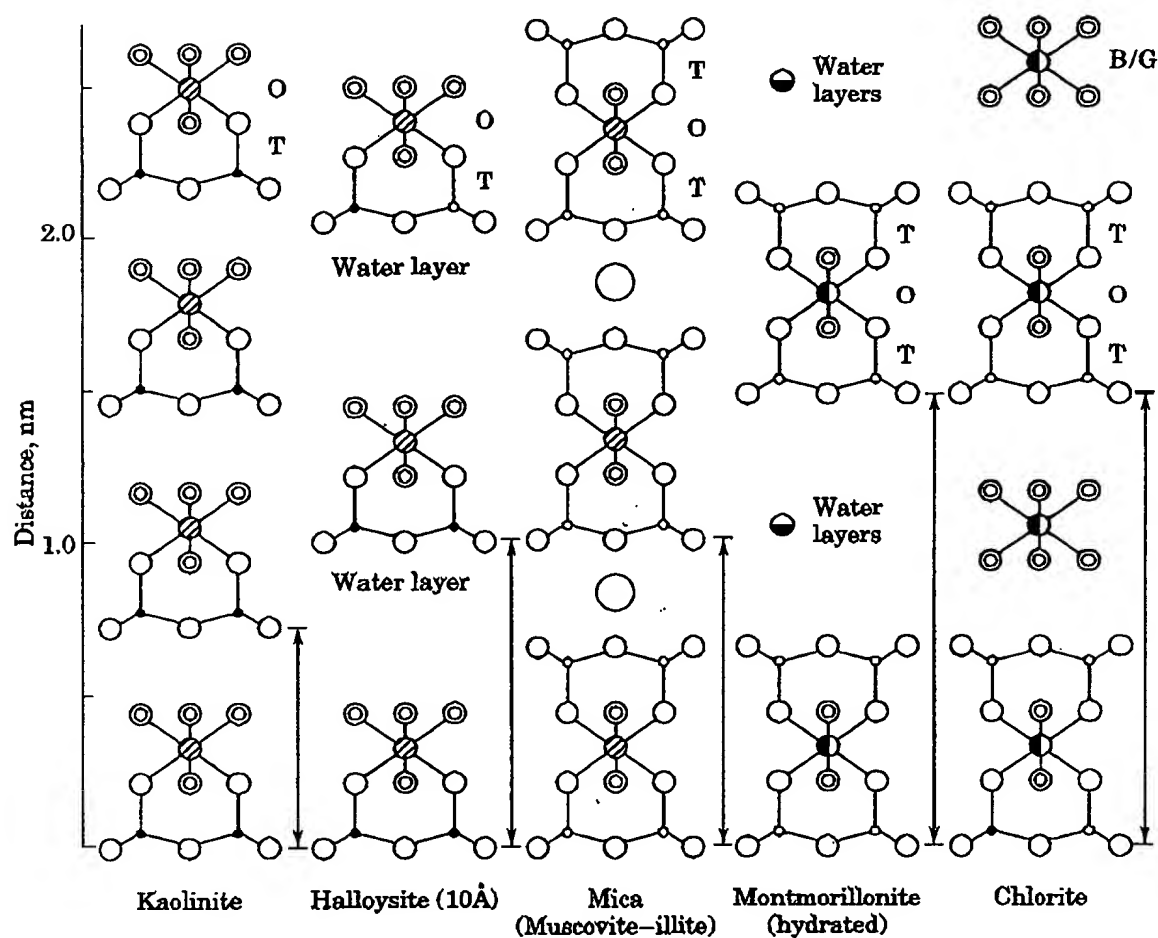
(1) Crystalline hydrated silicates of aluminum, iron, and magnesium comprise the majority of clay minerals, however, amorphous hydrated aluminum compounds are also included. Distinctions among clay minerals are made by chemical and structural parameters. The chemical variations range from kaolinite [1318-74-2], which is relatively uniform in chemical composition, to smectite minerals, which vary widely in chemical composition, base exchange properties, and expanding crystal lattice. The illite group, typically a component of sediment (9), includes micas, although illite [1273-60-3] differs from muscovite [1318-94-1],  $K_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2H_2O$ , because illite contains less potassium, and more water. The chlorite clay minerals resemble metamorphic chlorite [1318-59-8] (10), but aluminous or at least aluminum-rich chlorites have also been found in soils (4,11). Vermiculite [1318-00-9], characterized by a highly expanding crystal lattice, and sepiolite [15501-74-3],  $Mg_8Si_{12}O_{34}H_4$ , and palygorskite [12174-11-7], which possess chain or fiber structures, must also be included. Moreover, clay minerals are excellent examples of mixed layering, both random and regular, in layer-structure silicates. These mixed-layer clays are among the most ubiquitous of the various clay minerals. The structural differences among clay minerals are related to the arrangement of tetrahedral (T) and octahedral (O) layers, and the manner in which electrostatic charge imbalances, created by chemical substitution, are neutralized. Figure 1 shows several examples.

(2) The possible content of hydrated alumina and iron. Hydrated alumina minerals like gibbsite [14762-49-3],  $Al(OH)_3$ , boehmite [1318-23-6],  $AlOOH$ , and diasporite [14457-84-2],  $AlOOH$ , occur in bauxitic clays. Bauxites grade chemically into hydrated ferruginous and manganiferous laterites. Hence, finely divided  $M_2O_3$ , usually hydrated, may be a significant constituent of a clay where M may be Al or Fe. Hydrated colloidal silica may play a role in the slippery and sticky properties of certain clays.

(3) The extreme fineness of individual clay particles, which may be of colloidal size in at least one dimension. Clay minerals are usually platy in shape, and less often lathlike and tubular or scroll shaped (13). Because of this fineness clays exhibit the surface chemical properties of colloids (qv) (14). Some clays possess relatively open crystal lattices and show internal surface colloidal effects. Other minerals and rock particles, which are not hydrous aluminosilicates but which also show colloidal dimensions and characteristics, may occur intimately intermixed with the clay minerals and play an essential role.

(4) The property of thixotropy in various degrees of complexity (3). Thixotropic properties may lead to loss of stability as shown by the sometimes catastrophic flow of quick clays, especially in Norway, Sweden, and Canada (15).

(5) The possible content of quartz [14808-60-7],  $SiO_2$ , sand and silt, feldspars, mica [12001-26-2], chlorite, opal [14639-88-4], volcanic dust, fossil fragments, high density so-called heavy minerals, sulfates, sulfides, carbonate minerals, zeolites, and many other rock and mineral particles ranging upward in size from colloids to pebbles. An extreme example is that of a clay from western Texas composed of 98.5% dolomite [16389-88-1],  $CaMg(CO_3)_2$ , and 1.5% iron oxide and



**Fig. 1.** Diagrammatic representation of the succession of layers in some layer lattice silicates (12) where ○ is oxygen; ⊙, hydroxyl; \*, silicon; ♂, Si-Al; ⊗, aluminum; ●, Al-Mg; ○, potassium; ⊖, Na-Ca. Sample layers are designated as O, octahedral; T, tetrahedral; and B/G, brucite- or gibbsitelike. The distance depicted by arrows between repeating layers in nm are 0.72, kaolinite; 1.01, halloysite (10 Å); 1.00, mica; ca 1.5, montmorillonite; and 1.41, chlorite.

alumina; it occurs in rhombic particles averaging 0.008 mm in diameter, and possesses sufficient plasticity to be molded into bricklets (16).

The synthesis of clay minerals has been extensively studied in order to understand the genesis of clay minerals and more recently to calibrate analytical techniques (17-25). Many experiments were performed at high temperatures, some using synthetic chemicals, others using part naturally occurring minerals. Organic compounds were found to facilitate the synthesis of kaolinite at low temperature by condensing aluminum hydroxide into octahedrally coordinated sheets (18).

### Geology and Occurrence

Clays may originate through several processes: (1) hydrolysis and hydration of a silicate, ie, alkali silicate + water → hydrated aluminosilicate clay + alkali hy-

dioxide; (2) solution of a limestone or other soluble rock containing relatively insoluble clay impurities that are left behind; (3) slaking and weathering of shales (clay-rich sedimentary rocks); (4) replacement of a preexisting host rock by invading guest clay where the constituents are carried in part or wholly by solution; (5) deposition of clay in cavities or veins from solution; (6) bacterial and other organic activity, including the extraction of metal cations as nutrients by plants; (7) action of acid clays, humus, and inorganic acids on primary silicates; (8) alteration of parent material or diagenetic processes following sedimentation in marine and freshwater environments (26,27); and (9) resilication of high alumina minerals.

Clays or shales that may be utilized in the manufacture of bricks, tiles, and other heavy clay products exist in every state in the United States. (See BUILDING MATERIALS, SURVEY). Some blending of materials is often necessary to control shrinkage of the product, and the economics of manufacture are governed by the demands of fuel, labor, transportation costs, and the market.

Glacial clays, as unassorted glacial till or secondarily deposited melt water, are abundant in the United States north of the Missouri and Ohio Rivers. Quartz-rich sand, silt, or pebbles, especially limestone, may occur mixed with the clay. Kaolins are plentiful in North Carolina, South Carolina, Georgia (28), Florida, and Vermont. Certain flint clays and other clays having a kaolinitic composition which can replace kaolins in some uses (29), occur in Missouri, Arkansas, Colorado, Texas, Ohio, Indiana, Oregon, and Pennsylvania. Ball clays, ie, clays having high plasticity and strong bonding power, are obtained primarily from western Tennessee and Kentucky, though some are found in New Jersey. Other plastic clays, especially plastic fire clay, are extensively produced in Missouri, Illinois, Ohio, Kentucky, Mississippi, Alabama, and Arkansas.

Fire clays are those that resist fusion at a relatively high temperature, usually around 1600°C. Missouri, Pennsylvania, Ohio, Kentucky, Georgia, Colorado, New Jersey, Texas, Arkansas, Illinois, and Maryland are large producers of fire clays. Loess is a quartz-rich, clayey silt, windblown in origin but in some cases reworked by water. It is prevalent along the Missouri, Mississippi, and Ohio Rivers and their tributaries. Loess has been used primarily for brick making. Adobe, a calcareous, sandy to silty clay used extensively for making sundried brick, is available in the more arid southwestern states. Slip clay for glazing pottery is produced near Albany, New York.

Bentonite [1302-78-9], widely distributed geographically and geologically, also varies widely in properties. Swelling bentonite occurs in Wyoming, South Dakota, Montana, Utah, Nevada, and California. Bentonite that swells little or not at all occurs in large quantities in Texas, Arkansas, Mississippi, Kentucky, and Tennessee. Fuller's earth and bleaching clays are found chiefly in Georgia and Florida. Many of these fuller's earths contain palygorskite (locally called attapulgite) as the most important clay mineral constituent.

High alumina clays refer in the ceramic industries to nodular clays, burley-flint clay, burley and diaspor, gibbsitic or bauxitic kaolins (clays), abrasive clays, and others. Since the depletion of diaspor varieties in Missouri and Pennsylvania, most bauxitic kaolin and clay is produced in Alabama and Arkansas.

Each continent has clays of almost every type, however, certain deposits are outstanding (28-31). There are tremendous reserves of white kaolin in Brazil,

and deposits of bauxitic clay shared with countries across Brazil's northern borders. England has the famous kaolins of the Cornwall district. Refractory clays in Scotland provide the raw materials for a refractories (qv) industry. Similar deposits are found in Brittany and neighboring areas in France. Czechoslovakia and Germany have large reserves of kaolin accompanied by quartz and mica. There are large deposits of bauxitic clays (with bauxite) in Hungary and the former republics of Yugoslavia. Both flint clay and white kaolin are found in South Africa. Kaolins are found in the People's Republic of China. Japan has notable hydrothermal kaolins, sedimentary kaolin, smectite, and flint clay. Hydrothermal kaolins are also widely distributed in Mexico. Australia has large deposits of flint clay and kaolin clay naturally calcined by the burning of coal beds. New Zealand has hydrothermal clays. India has flint and lateritic clays. Sepiolite is found near Madrid, Spain. Localities producing bauxite almost always have a potential for producing associated high alumina clays.

The commercial value of a clay deposit depends on market trends, competitive materials, transportation facilities, new machinery and processes, and labor and fuel costs. Naturally exposed outcrops, geological area and structure maps, aerial photographs, hand and power auger drills, core drills, earth resistivity, and shallow seismic methods are used in exploration for clays (32). Clays are mined primarily by open-pit operation, including hydraulic extraction; however, underground mining is also practiced.

Specific information concerning the geology or occurrence of a particular deposit or variety of clay may be obtained from a state geological survey; general information may be obtained from the U.S. Geological Survey or the U.S. Bureau of Mines. Similar agencies may be contacted in foreign countries, or literature references may be consulted, eg, References 33-35, and the general references.

### Technological Classification

The technological classification of a clay (rock, deposit) should take into account the following factors: (1) the dominant clay mineral type including breakdown into its polymorphs, the sites and amount of charge on it, and shape of clay crystal and particle; (2) the clay minerals present in minor quantities, but perhaps coating the surface of the primary constituent; (3) the particle-size distribution of the clay and other minerals; (4) ion-exchange capacity and neutral molecule sorption; (5) the type of exchangeable ions present on the clay and degree of saturation of exchange sites; (6) hygroscopicity of the clay; (7) reactivity of the clay with organic compounds; (8) expansion potentialities of the clay mineral lattice; (9) electrolytes and solutions in association with the clay deposit; (10) the accessory minerals, or mineral impurities, their sizes, homogeneity of mixture, and ion-exchange capacity; (11) content of organic matter and especially its occurrence, size and discreteness of particles, its adsorption on and/or within the clay crystal units, and protective colloidal action; (12) presence or absence of bacteria or other living organisms because organic growth may rapidly change the pH and other properties of a clay deposit; (13) content of hydrated alumina and/or silica, which are relatively soluble in ground water or in dilute acid or alkali; (14) the structure and texture of the clay deposit, such as lamination, orientation of mineral parti-

cles, and other gross features; (15) the rheological properties of both the natural and processed clay; and (16) the engineering strength and sensitivity to moisture, desalination, and shock, eg, the quick clays.

### Mineralogy

The development of apparatus and techniques, such as x-ray diffraction, contributed greatly to research on clay minerals. Crystalline clay minerals are identified and classified (36) primarily on the basis of crystal structure and the amount and locations of charge (deficit or excess) with respect to the basic lattice. Amorphous (to x-ray) clay minerals are poorly organized analogues of crystalline counterparts.

The structural variations among the clay minerals can be understood by considering various physical combinations of tetrahedral and octahedral sheets and the electrostatic effect chemical substitution has on the structural units. The tetrahedral sheets are composed primarily of  $\text{Si}^{4+}$  and oxygen, but minor amounts of  $\text{Al}^{3+}$  or  $\text{Fe}^{3+}$  may substitute for  $\text{Si}^{4+}$ . The substitution of  $\text{M}^{3+}$  for  $\text{Si}^{4+}$  leaves the tetrahedral sheet negatively charged. The cations of the octahedral sheet are composed primarily of  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Fe}^{2+}$ , but all other transition elements, except Sc, may be included. The anions of the octahedral sheet are  $\text{O}^{2-}$ ,  $\text{OH}^-$ , and  $\text{F}^-$ . The smallest unit of the octahedral sheet contains three octahedra having an ideal net charge of negative six, ie, three  $\text{O}^{2-}$ . If the negative charge is balanced by two trivalent cations, the layer is referred to as a dioctahedral layer; if balanced by three bivalent cations, the layer is referred to as a trioctahedral layer. Substitution of bivalent cations for trivalent cations, univalent cations ( $\text{Li}^+$ ) for bivalent cations or unfilled octahedral sites, leaves the octahedral layer a net negative charge. The tetrahedral apical oxygen is shared with the octahedral layer to join the two types of layers (37,38).

The least complicated clay minerals are the 1:1 clay minerals composed of one tetrahedral (T) layer and one octahedral (O) layer (see Fig. 1). These 1:1 clay minerals are also referred to as TO minerals. The TO package has a basal spacing (nominal thickness) of 0.7 nm (7 Å) and they are commonly referred to as 7 Å minerals. Kaolinite, the dioctahedral 1:1 mineral, has  $\text{Al}^{3+}$  filling two of three octahedral sites, and serpentine [12168-92-2],  $(\text{Mg})_3\text{Si}_2\text{O}_5(\text{OH})_4$ , the trioctahedral 1:1 mineral has  $\text{Mg}^{2+}$  filling all three octahedral sites. The kaolin minerals have limited substitution in the octahedral layer and have negligible layer charge, as do most of the serpentine minerals. The net electrostatic charge, referred to as  $x$  is approximately zero for kaolin and serpentine minerals. A group of serpentine minerals have significantly paired substitution, eg,  $\text{Al}^{3+}$  in both the tetrahedral and octahedral layers, but still maintain electrostatic neutrality.

Clay minerals that are composed of two tetrahedral layers and one octahedral layer are referred to as 2:1 clay minerals or TOT minerals. The apical oxygens of the two tetrahedral sheets project into the octahedral sheet. The 2:1 structure has a basal spacing (nominal thickness) of 1.0 nm (10 Å). Pyrophyllite [12269-78-2],  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$ , is the dioctahedral mineral, ie,  $\text{Al}^{3+}$  in the octahedral sites, and talc [14807-96-6],  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$ , is the trioctahedral, ie,  $\text{Mg}^{2+}$  in the octahedral sites. Both these minerals are essentially free of substitution in the

octahedral site and therefore do not have a net charge deficit ( $x = 0$ ) in the TOT layer.

The multitude of variation in clay minerals is caused by substitution in the octahedral and tetrahedral layers resulting in charge deficits. The manner in which the charge deficit is balanced leads to many of the useful and unique properties of clay minerals.

The smectite minerals, where the charge deficit is balanced by loosely held hydrated cations in the interlayer space between 2:1 layers, have the smallest charge deficit,  $x = 0.2-0.6$ . Smectite minerals may be dioctahedral or trioctahedral depending on the predominant cation in the octahedral layer. The amount of water in the interlayer space varies with the cation content and the basal spacing may vary between 1.0–1.8 nm (10–18 Å). Vermiculite has a charge deficit  $> 0.6$ . The deficit is balanced by cations with two water layers and has a basal spacing of 1.4 nm (14 Å). Illite has a net negative charge of  $\approx 0.9$  and the charge deficit is balanced by  $K^+$ . The  $K^+$  ion fits nearly perfectly into the basal tetrahedral plane and the resulting structure has a basal spacing of approximately 1.0 nm (10 Å). The basal spacing cannot be easily altered by common chemical treatments designed to identify clay minerals in x-ray analysis. Glauconite [1317-57-3] is an Fe-rich dioctahedral mica similar to illite. The mica minerals, eg, muscovite, biotite, etc, have  $x \approx 1.0$  and balance the charge deficit using  $K^+$  in a manner similar to illite. Chlorite minerals also have  $ca\ x = 1$ , and the charge deficit is balanced by the inclusion of a Mg or Al hydroxide layer that has a net positive charge of approximately 1.0. The chlorite minerals are composed of 2:1 layers plus an interlayer hydroxide sheet yielding a 1.4 nm (14 Å) basal spacing.

Palygorskite and sepiolite minerals are 2:1 layered phyllosilicates that differ from the above mentioned clays because the octahedral sheets have significant intracrystalline void space caused by discontinuous octahedral layers. The basal tetrahedral unit is connected to an adjacent inverted basal tetrahedral creating a void space or channel. Charge deficits are balanced by hydrated cations in the intracrystalline space.

Mixed-layer clays are a combination of minerals, with the exception of palygorskite and sepiolite. Mixed-layer minerals may contain equal proportions of or may be dominated by one mineral. The arrangement of the component minerals may be random, short-range ordered, or long-range ordered. In the case of illite-smectite many studies have demonstrated a complete range of compositions varying from dominantly smectite through equal amounts of smectite and illite components, to dominantly illite, with increasing temperature and/or depth of the sediment. A more detailed discussion of the structure of clay minerals is available (37–40).

Various techniques are used to study crystalline clay minerals. These include: the polarizing microscope (41), chemical analysis and computation of the mineral formula taking into account the substitution of atoms (37,42,43), staining (44–46), density, possible electrical double refraction (47,48), dehydration, base exchange (49,50), electron micrographs, transmission electron microscopy (tem) (51–53) scanning electron microscopy (sem) (54–57), energy-dispersive x-ray spectral (edxs) microanalysis (58), scanning tunneling microscopy (stm) (59), atomic force microscopy (afm) (59–61), analytical transmission electron microscopy (atem) (62–64), x-ray or electron powder diffraction patterns (xrd)

(36,43,65,66), differential thermal analysis (dta) and thermal balance analysis (tga), imbibition (67–69), high pressure dta (70), infrared absorption (49,51,71–74), magic-angle spin nuclear magnetic resonance (mas/nmr) spectroscopy and solid-state nmr (75–77), electron paramagnetic resonance (78), Mössbauer spectroscopy (78–80), and field appearance, especially responses to weathering (81, and the general references) (see ANALYTICAL METHODS).

Clay minerals are divided into crystalline and paracrystalline groups and a group amorphous to x-rays. Although the clays of the different groups are similar, they show vastly different mineralogical, physical, thermal, and technological properties (3). Chemical analysis alone has limited value in revealing the clay's identity or usefulness. The mineral composition, which reveals the organization of the constituent elements is most important.

### Crystalline and Paracrystalline Groups

**Kaolins.** The kaolin minerals include kaolinite [1318-74-7], dickite [1318-45-2], and nacrite [12279-65-1] which all have composition  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ; halloysite (7 Å) [12069-16-1],  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ , and halloysite (10 Å) [12244-16-5],  $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 4\text{H}_2\text{O}$  (82–85). The structural formulas for kaolinite and halloysite (10 Å), which are shown in Figure 1, are  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$  and  $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ , respectively. The so-called fire clay mineral is a *b*-axis disordered kaolinite (12); halloysite (7 Å) and halloysite (10 Å) are disordered along both the *a*- and *b*-axes. Indeed, most variations in the kaolin group originate as structural polymorphs, related to variations in layer stacks. Representative analyses (82–84) of the kaolin minerals are given in Table 1.

Kaolinite and dickite are easily distinguished where they occur in recognizable crystals (87). Nacrite is relatively rare. Halloysite (7 Å) is usually exceedingly fine-grained, showing a mean index of refraction of about 1.546. The index of refraction for halloysite (10 Å) varies somewhat with the immersion liquid used; it ranges from 1.540 to 1.552 (83).

X-ray studies show that kaolin minerals have two-layer crystal structures: a sheet of silica tetrahedra and an alumina–gibbsitelike sheet. Adjacent cells are spaced about 0.71 nm across the (001) plane. The interplanar spacings normal to the (001) cleavage are the most significant criteria used in x-ray differentiation between the clay mineral groups. Within the kaolin group other x-ray structural differences are used to distinguish the members (12). The kaolin minerals are dioctahedral minerals and therefore only two of the three octahedral sites are filled. In kaolinite the vacant octahedral site is either always the B site or the C site giving kaolinite a one-layer triclinic structure (88,89). In dickite, the vacancy alternates regularly between the B and C sites giving dickite a two-layer monoclinic structure (88). Nacrite is an uncommon mineral that has a six-layer monoclinic structure with an inclined *z*-axis.

Halloysite, a mineral in the kaolin family, has a chemical composition similar to, but physical properties that differ greatly from, kaolinite. Halloysite differs from kaolinite in tetrahedral Al content, layer stacking sequence, and configuration of the six-fold rings (90). Earlier work referred to the hydrated form of halloysite as endellite [11244-16-1] (83). This is a naturally occurring 1.0 nm min-



**Table 1. Chemical Analyses of the Kaolin Minerals, wt %**

Component	Sample					
	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>d</sup>	5 <sup>e</sup>	6 <sup>f</sup>
SiO <sub>2</sub>	45.44	40.26	46.5	45.78	42.68	44.90
Al <sub>2</sub> O <sub>3</sub>	38.52	37.95	39.5	36.46	38.49	38.35
Fe <sub>2</sub> O <sub>3</sub>	0.80	0.30		0.28	1.55	0.43
FeO			1.08			
MgO	0.08			0.04	0.08	trace
CaO	0.08	0.22		0.50		trace
K <sub>2</sub> O	0.14	0.74		0.25	0.49	0.28
Na <sub>2</sub> O	0.66				0.28	0.14
TiO <sub>2</sub>	0.16				2.90	1.80
H <sub>2</sub> O loss						
at 105°C	0.60	4.45		2.05		
above 105°C	13.60	15.94	14.0	13.40	14.07	14.20
<i>Total</i>	<i>100.08</i>	<i>99.86</i>	<i>100.0</i>	<i>99.84</i>	<i>100.54</i>	<i>100.10</i>

<sup>a</sup>Kaolinite, Roseland, Va. (84).<sup>b</sup>Halloysite, Huron Co., Ind. (82).<sup>c</sup>Theoretical kaolinite.<sup>d</sup>Washed kaolin, Webster, N.C. (6).<sup>e</sup>Flint fire clay, near Owensville, Mo. (86)<sup>f</sup>Typical sedimentary kaolin, S.C. Ga., Ala. Courtesy S. C. Lyons.

eral having loosely bound water responsible for expansion to 1.0 nm along the *c*-axis. This mineral, referred to as halloysite (10 Å) (91), can also be expanded to 1.0 nm when solvated in ethylene glycol. If halloysite (10 Å) is dehydrated its *c*-axis dimension is reduced to 0.7 nm. It then becomes halloysite (7 Å) and its *c*-axis dimension is not able to rehydrate to 1.0 nm.

Four basic morphologies of halloysite are recognized: tubular (long and short), spheroidal, platy, and prismatic. Tubular halloysite is formed in order to compensate for the lateral misfit between the larger tetrahedral and the smaller octahedral sheets (13,90). An alternative interpretation is that certain crystals have an inherent roundish, elongate morphology (92). In platy halloysite the lateral misfit is relieved by the substitution of the larger Fe<sup>3+</sup> for octahedral Al<sup>3+</sup>. Spheroidal halloysite is a result of the dissolution-precipitation of amorphous particles, commonly volcanic glass and pumice. There is no consensus concerning the origin of prismatic halloysite (90). The substitution of Al in the tetrahedral layer is a function of the pH of the liquid medium during formation (93). Aluminum, bound by water in octahedral coordination at relatively low pH levels, is readily incorporated into the octahedral sheets of 1:1 minerals and as a result kaolinite is formed. In a pH range from 5.3 to 6 at 25°C, or 4 to 5 at 100°C, aluminum coordination changes from octahedral to tetrahedral. The change in aluminum coordination enables Al<sup>3+</sup> to substitute for Si<sup>4+</sup> in the tetrahedral sheet, leading to a charge imbalance in the crystal structure that is satisfied by cations in bound water. The substitution of Al<sup>3+</sup> for Si<sup>4+</sup> also leads to a misfit between octahedral and tetrahedral layers. In other kaolin group minerals, any misfit between octahedral and tetrahedral layers is compensated by tetrahedral



rotation; however, the cations in the bound water of halloysite prevent tetrahedral rotation, and the misfit is compensated by the rolling of the tetrahedral sheet to the octahedral sheet. Rolling brings tetrahedral and octahedral cations into close proximity and water helps to reduce cation-cation Coulomb repulsion forces (90).

Halloysite may be differentiated from kaolinite and dickite by treatment with potassium acetate, ethylene glycol, formamide, and hydrazine (54,94). Staining kaolin minerals with aniline dyes produces varied artificial pleochroism which may be sufficiently selective to identify particular mineral species (45). In differential thermal analysis, kaolinite shows a strong endothermic peak at about 620°C and a strong exothermic peak at about 980°C, which sharply differentiates it from other clay mineral groups. Electron micrographs show kaolinite in roughly equidimensional pseudohexagonal plates and halloysite most commonly as lath-shaped tubes. Halloysite may also have platy, prismatic, or spherical shapes (90). Kaolinite, the most abundant, and halloysite, the second most abundant, of the kaolin group minerals are the most used by industry. Problems of clay mineral differentiation for the kaolin group rarely arise; however, adequate means for identifying and distinguishing various species are available (34,45,94,95). The cationic base-exchange capacity (CEC) of kaolinite is low, less than 10 meq/100 g of dry clay; the CEC of halloysite has been reported to be as high as 60 meq/100 g (96).

Kaolin most commonly originates by the alteration of feldspar or other aluminum silicates via an intermediate solution phase (97,98) usually by surface weathering (26,99) or by rising warm (hydrothermal) waters. A mica, or hydrated alumina solid may form as an intermediate phase during the alteration from parent material to kaolin minerals.

Large deposits of relatively pure kaolinite have developed from parent, feldspar-rich pegmatites, whereas others are secondarily deposited in sedimentary beds after transportation. Colloidal fractions of geologically ancient soils were presumably concentrated in old swamps and leached to develop kaolinitic clay deposits (6,29). Kaolinite is formed by weathering in an oxidizing environment under acid conditions, and in a reducing environment where bases such as calcium, magnesium, alkalies, and iron(II) are removed. Removal of the bases is essential in kaolin formation (100). With more intense leaching of silica from the clay an aluminous hydrate remains and the clay becomes bauxitic. Kaolinite may develop from the silication of gibbsite (7). Halloysite may be formed either by hydrothermal or weathering processes. Allophane [12172-71-3] may have led to halloysite and thence to kaolinite as crystallization became more highly ordered following weathering (101); however, this sequence does not always prevail. Some indications point toward a possible association of acid sulfate waters and mobile potassium for the origin of halloysite (99). The relationship between pH and aluminum coordination and the formation of either kaolinite or halloysite (93) has been demonstrated. The fact that aluminum may be either tetrahedrally coordinated and a precursor to halloysite, or octahedrally coordinated and a precursor to kaolinite, makes it possible that one may form from the other.

The textures of kaolin (rock) include varieties similar to examples observed in igneous and metamorphic as well as sedimentary rocks (98). Kaolin grains and crystals may be straight or curved, sheaves, flakes, face-to-face or edge-to-edge floccules, interlocking crystals, tubes, scrolls, fibers, or spheres. (98). The kaolin

group is transformed at high temperatures to a silica-alumina spinel structure (102), thence to mullite [1302-93-8],  $\text{Al}_6\text{Si}_2\text{O}_{13}$ , with or without accompanying cristobalite [14464-46-1],  $\text{SiO}_2$ , (103,104). The alkali metal, flux, and content of kaolin clay strongly influence the phases formed upon heating.

**Serpentines.** Substituting 3  $\text{Mg}^{2+}$  for the 2  $\text{Al}^{3+}$  in the kaolin structure results in the serpentine minerals,  $\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$ . In serpentines all three possible octahedral cation sites are filled. Most serpentine minerals are tubular to fibrous in structure presumably because of misfit between Mg octahedral and tetrahedral layers. Different varieties of magnesium serpentine are recognized as resulting from the different structures that have evolved to accommodate the misfit between the size of the octahedral and tetrahedral sheets. Lizardite [12161-84-1] results from a 1:1 planar layer structure; chrysotile [12001-27-5] from a cylindrical curvature of the layers; antigorite [66076-98-0] from a curvature of alternating wave modulation; and carlosturanite [98443-44-8] from ordered vacancies and modifications of the tetrahedral sheet within a planar structure (105).

Chrysotile (serpentine) occurs in both clino and ortho structures. Both one-layer ortho and clino, and six-layer ortho (as in nacrite) structures have been observed. Chrysotile transforms at high temperature to forsterite [15118-03-3] and silica. Particularly fibrous varieties are called asbestos (qv).

A number of serpentine group minerals have substitutions in both the tetrahedral and octahedral layer, but they still maintain electrostatic neutrality. Amestite [12413-27-5], which approximates  $(\text{Mg}_2\text{Al})(\text{SiAl})\text{O}_5(\text{OH})_4$  in composition, cronstedite [61104-43-3],  $(\text{Fe}_2^{2+}, \text{Fe}^{3+})(\text{SiFe}^{3+})\text{O}_5(\text{OH})_4$ , chamosite, [12173-07-2],  $(\text{Fe}^{2+}, \text{Fe}^{3+})_{2.3}(\text{Fe}^{2+}, \text{Al})_{0.7}(\text{Si}_{1.14}\text{Al}_{0.86})\text{O}_5(\text{OH})_4$ , and berthierine [12178-37-9],  $(\text{Fe}^{2+}, \text{Fe}^{3+}, \text{Mg})_{2.3}(\text{Si}, \text{Al})_2\text{O}_5(\text{OH})_4$ , are examples of such minerals (105). Garnierite [12198-10-6], a general term for hydrous nickel silicates, probably falls in this class of serpentine group minerals. Also, a cobalt serpentine has been synthesized (12).

**Talc and Pyrophyllite.** Talc (qv) and pyrophyllite are 2:1 layer clay minerals having no substitution in either the tetrahedral or octahedral layer. These are electrostatically neutral particles ( $x = 0$ ) and may be considered ideal 2:1 layer hydrous phyllosilicates. The structural formula of talc, the trioctahedral form, is  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  and the structural formula of pyrophyllite, the dioctahedral form, is  $\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$  (106). Ferripyrophyllite has the same structure as pyrophyllite, but has ferric iron instead of aluminum in the octahedral layer. Because these are electrostatically neutral they do not contain interlayer materials. These minerals are important in clay mineralogy because they can be thought of as pure 2:1 layer minerals (106).

Talc and pyrophyllite are found in metamorphic rocks that are rich in Mg and Al, respectively. Talc is most common in metamorphosed ultrabasic rocks and in metamorphosed siliceous dolomite. Pyrophyllite is found in metapelites, including metabauxites and metakaolinites, and in rocks enriched in Al by hydrothermal processes (106).

**Smectites (Montmorillonites).** Smectites are the 2:1 clay minerals that carry a lattice charge and characteristically expand when solvated with water and alcohols, notably ethylene glycol and glycerol. In earlier literature, the term montmorillonite was used for both the group (now smectite) and the particular member of the group in which Mg is a significant substituent for Al in the octa-

hedral layer. Typical formulas are shown in Table 2. Less common smectites include volkhonskoite [12286-87-2] which contains  $\text{Cr}^{2+}$ ; medmontite [12419-74-8],  $\text{Cu}^{2+}$ ; and pimelite [12420-74-5],  $\text{Ni}^{2+}$  (12).

Smectites are structurally similar to pyrophyllite [12269-78-2] or talc [14807-96-6], but differ by substitutions mainly in the octahedral layers. Some substitution may occur for Si in the tetrahedral layer, and by F for OH in the structure. Deficit charges in smectite are compensated by cations (usually Na, Ca, K) sorbed between the three-layer (two tetrahedral and one octahedral, hence 2:1) clay mineral sandwiches. These are held relatively loosely, although stoichiometrically, and give rise to the significant cation exchange properties of the smectite. Representative analyses of smectite minerals are given in Table 3. The determination of a complete set of optical constants of the smectite group is usually not possible because the individual crystals are too small. Representative optical measurements may, however, be found in the literature (42,107).

X-ray diffraction patterns yield typical 1.2–1.4 nm basal spacings for smectite partially hydrated in an ordinary laboratory atmosphere. Solvating smectite in ethylene glycol expands the spacing to 1.7 nm, and heating to 550°C collapses it to 1.0 nm. Certain micaceous clay minerals from which part of the metallic interlayer cations of the smectites has been stripped or degraded, and replaced by  $\text{H}_3\text{O}^+$ , expand similarly. Treatment with strong solutions of potassium salts may permit differentiation of these expanding clays (108).

Smectite [12199-37-0] from an oxidized outcrop is stained light blue by a dilute solution of benzidine hydrochloride. The color does not arise from smectite specifically, but from reaction of a high oxidation state of elements such as  $\text{Fe}^{3+}$  or  $\text{Mn}^{4+}$  (46).

Transmission electron micrographs show hectorite and nontronite as elongated, lath-shaped units, whereas the other smectite clays appear more nearly equidimensional. A broken surface of smectite clays typically shows a "corn flakes" or "oak leaf" surface texture (54). High temperature minerals formed upon heating smectites vary considerably with the compositions of the clays. Spinels commonly appear at 800–1000°C, and dissolve at higher temperatures. Quartz, especially cristobalite, appears and mullite forms if the content of aluminum is adequate (38).

**Table 2. Formulas of Smectite Minerals<sup>a</sup>**

Mineral	CAS Registry Number	Formula <sup>b</sup>
montmorillonite	[1318-93-01]	$[\text{Al}_{1.67}\text{Mg}_{0.33}(\text{Na}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH})_2]$
beidellite	[12172-85-9]	$\text{Al}_{2.17}[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.17}\text{O}_{10}(\text{OH})_2]$
nontronite	[12174-06-0]	$\text{Fe(III)}[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2]$
hectorite	[12173-47-6]	$[\text{Mg}_{2.67}\text{Li}_{0.33}(\text{Na}_{0.33})\text{Si}_4\text{O}_{10}(\text{OH},\text{F})_2]$
saponite	[1319-41-1]	$\text{Mg}_{3.00}[\text{Al}_{0.33}(\text{Na}_{0.33})\text{Si}_{3.67}\text{O}_{10}(\text{OH})_2]$
sauconite	[12424-32-7]	$[\text{Zn}_{1.48}\text{Mg}_{0.14}\text{Al}_{0.74}\text{Fe(III)}_{0.40}][\text{Al}_{0.99}\text{Si}_{3.01}\text{O}_{10}(\text{OH})_2\text{X}_{0.33}]$

<sup>a</sup>Ref. 42.

<sup>b</sup>More substitution takes place than shown;  $\text{Na}_{0.33}$  or  $\text{X}_{0.33}$  refers to the exchangeable base (cation) of which 0.33 equivalent is a typical value.

**Table 3. Chemical Analyses of the Smectite Minerals, wt %**

Component	Sample					
	1 <sup>a</sup>	2 <sup>b</sup>	3 <sup>c</sup>	4 <sup>d</sup>	5 <sup>e</sup>	6 <sup>f</sup>
SiO <sub>2</sub>	51.14	47.28	43.54	55.86	42.99	34.46
Al <sub>2</sub> O <sub>3</sub>	19.76	20.27	2.94	0.13	6.26	16.95
Fe <sub>2</sub> O <sub>3</sub>	0.83	8.68	28.62	0.03	1.83	6.21
FeO			0.99		2.57	
MnO	trace			none	0.11	
ZnO	0.10					23.10
MgO	3.22	0.70	0.05	25.03	22.96	1.11
CaO	1.62	2.75	2.22	trace	2.03	
K <sub>2</sub> O	0.11	trace		0.10	trace	0.49
Na <sub>2</sub> O	0.04	0.97		2.68	1.04	
Li <sub>2</sub> O				1.05		
TiO <sub>2</sub>	none			none		0.24
P <sub>2</sub> O <sub>6</sub>						
F				5.96		
H <sub>2</sub> O removed						
at 150°C	14.81	19.72	14.05	9.90	13.65	6.72
above 150°C	7.99		6.62	2.24	6.85	10.67
<i>Total</i>	<i>99.75</i>	<i>100.37</i>	<i>100.02</i>	<i>102.98</i>	<i>100.29</i>	<i>99.95</i>

<sup>a</sup>Montmorillonite, Montmorillon, France (42).<sup>b</sup>Beidellite, Beidell, Colo. (42).<sup>c</sup>Nontronite, Woody, Calif. (42).<sup>d</sup>Hectorite, Hector, Calif. (42).<sup>e</sup>Saponite, Ahmeek Mine, Mich. (107).<sup>f</sup>Sauconite, Friedensville, Pa. (107).

The cation-exchange capacity of smectite minerals is notably high, 80–90 meq or higher per 100 g of air-dried clay, and affords a diagnostic criterion of the group. The crystal structure is obviously weakly bonded. Moreover, the structure of smectite is expandable between the silicate layers so that when the clay is soaked in water it may swell to several times its dry volume (eg, bentonite clays). Soil colloids having high cation-exchange capacity facilitate the transfer of plant nutrients to absorbing plant rootlets.

The minerals of the smectite group have been formed by surface weathering, low temperature hydrothermal processes, alteration of volcanic dust in stratified beds (109), action of circulating water of uncertain source along fractures and in veins, and laboratory synthesis. The optimum weathering environment for smectite genesis is one in which calcium, iron(II), and especially magnesium are present in significantly high concentrations. Potassium should be low or low in relation to magnesium, calcium, and ferrous iron. Organic matter that exerts reducing action is usually concomitant, and a neutral to slightly alkaline medium generally prevails under conditions where the alkali and alkaline-earth metals are not readily removed. The weathering environment for smectite is different from that in which kaolinite is formed (100). If the system permits effective leach-

ing and  $H^+$  ions become available in sufficient quantity to cause the metallic cations to be easily leached away, kaolinite tends to form. The reverse reaction rarely, if ever, takes place.

Bentonite is a rock rich in montmorillonite that has usually resulted from the alteration of volcanic dust (ash) of the intermediate (latitic) siliceous types. In general, relicts of partially unaltered feldspar, quartz, or volcanic glass shards offer evidence of the parent rock. Most adsorbent clays, bleaching clays, and many clay catalysts are smectites, although some are palygorskite [1337-76-4].

Pillared clays are smectite minerals or illite-smectite minerals that have been structurally modified to contain pillars of stable inorganic oxide. The pillars prop open the smectite structure so they have a basal space of approximately 3.0 nm. Typical metals in the pillars include Al, Zr, Ti, Ce, and Fe, and these materials are used in catalytic processes to crack heavy crude oils (110-112).

The original pillared clays were made by: (1) mixing smectite with a polymeric cationic hydroxy metal complex such as aluminum chlorhydrol; (2) allowing a minimal amount of time for the cationic hydroxy metal complex to exchange with the interlayer cations; and (3) calcining the resulting material to decompose the hydroxy metal complex (110). A number of newer methods have been developed to make pillared clays (111-117).

**Illite.** Illite is a general term for the clay mineral constituents of argillaceous sediments that strongly resemble mica minerals (9,118). Other names that have been used for illite include: bravaisite [12197-39-6], degraded mica, hydromica, hydromuscovite [12173-60-3], hydrous illite, hydrous mica, K-mica, micaceous clay, and sericite [12174-53-7] (37). Illite and the mica minerals have a 2:1 sheet structure similar to the smectite minerals except that the maximum charge deficit in mica is typically in the tetrahedral layers and contains potassium held tenaciously in the interlayer space, which contributes to a 1.0 nm basal spacing. Illite differs from mica minerals in the following ways: (1) one-sixth of the  $Si^{4+}$  tetrahedral sites of illite are replaced by  $Al^{3+}$  compared to one-fourth in mica minerals; (2) illite has a net charge deficiency of 1.3 per unit cell compared to 2.0 for mica minerals; (3) illite has a higher silica to alumina ratio than mica minerals; (4) in illite, the potassium ions between the unit layers may be partially replaced by other cations, possibly  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $H^+$ , whereas, in the mica minerals the interlayer ion is almost exclusively potassium; (5) illite crystals contain some randomness in the stacking of the layers in the  $c$  direction; and (6) the size of the illite particles occurring naturally is very small, of the order of 1 to 2  $\mu m$  or less (38). Because the mica minerals and illite in argillaceous sediments may be widely diverse in origin, considerable variations exist in the composition and polymorphism of the illite minerals including trioctahedral illites, sodium illite (brammallite [12197-36-3]), and ammonium illite (118).

The formula of illite can be expressed as  $2K_2O \cdot 3MO \cdot 8R_2O_3 \cdot 24SiO_2 \cdot 12H_2O$  (9), and the crystal structure (119) by the formula  $K_y[Al_{4-x}(Fe,Mg)_x](Si_{(8-y)+x}Al_y)O_{20}(OH)_4$  where  $y$  refers to the  $K^+$  ions that satisfy the excess charges resulting when about 15% of the  $Si^{4+}$  positions are replaced by  $Al^{3+}$ . A representative chemical analysis of illite is found in Table 4. Optical constants of illite minerals are difficult to obtain because of the small size of the available crystals. The highest ( $\gamma$ ) index of refraction ranges from about 1.588 to 1.610, the

**Table 4. Chemical Analysis of Illite, Glauconite, and Attapulgite, wt %**

Component	Illite	Glauconite	Attapulgite
SiO <sub>2</sub>	51.22	48.66	55.03
Al <sub>2</sub> O <sub>3</sub>	25.91	8.46	10.24
Fe <sub>2</sub> O <sub>3</sub>	4.59	18.8	3.53
FeO	1.70	3.98	
MgO	2.84	3.56	10.49
CaO	0.16	0.62	
K <sub>2</sub> O	6.09	8.31	0.47
Na <sub>2</sub> O	0.17		
TiO <sub>2</sub>	0.53		
H <sub>2</sub> O removed			
at 110°C	7.49		
at 150°C			9.73
above 150°C			10.13
<i>Total</i>	<i>100.7</i>	<i>99.8</i>	<i>99.62</i>

birefringence is about 0.033, the optical character is negative, and the axial angle,  $2V$ , is small, on the order of  $5^\circ$ .

A 1.0 nm basal spacing exhibited in a diffractogram peak that is somewhat broad and diffuse and skewed toward wider spacings characterizes the x-ray diffraction pattern of illite. Polymorphs may be present (120). Muscovite derivatives are typically dioctahedral; phlogopite derivatives are trioctahedral.

Differential thermal analysis curves of illite show three endothermic peaks in the ranges 100–150, 500–650, and at about 900°C, and an exothermic peak at about 940°C, or immediately following the highest endothermic peak. Minerals formed from illite at high temperature vary somewhat with the composition of the clay, but usually a spinel-structure mineral followed by mullite at still higher temperatures is observed (42). The cation-exchange capacity of illite is 20–30 meq/100 g of dry clay. The interlayer potassium exerts a strong bond between adjacent clay structures. Illite that has lost part of its original potassium by weathering processes may be reconstituted with the sorption and incorporation of transient dissolved potassium (108).

Illite was defined as the most abundant clay mineral in Paleozoic shale and is widespread in many other sedimentary rocks; it is common in soils, slates, certain alteration products of igneous rocks, and recent sediments. Its origin has been attributed to alteration of silicate minerals by weathering and hydrothermal solutions, reconstitution, wetting and drying of soil clays, and diagenesis involving other three-layer minerals and potassium during geologic time and pressure under deep burial (27,121,122). Illitization of smectite via illite–smectite mixed-layer intermediates is a very common and an important reaction in the formation of shales during burial diagenesis.

**Glauconite.** Glauconite [1317-57-3] (123–126) is a green, dioctahedral, micaceous clay rich in ferric iron and potassium. The generally accepted formula for glauconite is  $(\text{Na},\text{K})_{0.78}(\text{Fe}^{3+}_{1.01}\text{Al}_{0.45}\text{Mg}_{0.39}\text{Fe}^{2+})_{2.05}(\text{Si}_{3.65}\text{Al}_{0.35})\text{O}_{10}(\text{OH})_2$  (39). Glauconite has many characteristics common to illite, but much glauconite con-

tains random mixed expanding layers, and can be referred to as interstratified glauconite-smectite minerals (127). In addition, glauconite found in Late Cenozoic rocks tends to have less crystallographic order than older glauconite; therefore, the modifiers ordered (well crystalline) and disordered (poorly crystalline) are commonly used (39,127). Prior to the 1950s the term glauconite was used for any type of green-colored sedimentary rocks or for green-colored grains, therefore the term glauconite in early literature differs in usage (127).

Glauconite occurs abundantly in sand-size or bigger pellets, or in pellets within fossils, notably foraminifera, giving it an organic connotation (12). Occurrences as replacements, and matrix and flakes in sandstone as a product of diagenesis (121,128), indicate other possible origins. Glauconite is typically formed in a marine environment (129), but glauconitic mica has been reported from non-marine rocks (81,130).

The chemical analysis of glauconite (Bonneterre, Missouri), is given in Table 4. Powder x-ray diffraction patterns resemble those of illite in which intensities of even-numbered basal spacings are minimal. The glauconitic green sands of New Jersey have been used in ion-exchange, water-softening installations (see ION EXCHANGE), and as a source of slowly released potassium in soil amendments.

Celadonite [71606-04-7] is an iron-rich dioctahedral micaceous mineral that is similar to glauconite. Celadonite has a composition of:  $(\text{Na,K})_{0.83}(\text{Fe}^{3+}_{0.72}\text{Al}_{0.49}\text{Mg}_{0.63}\text{Fe}^{2+}_{0.20})_{2.05}(\text{Si}_{3.81}\text{Al}_{0.19})\text{O}_{10}(\text{OH})_2$  (39) and, like glauconite, has well crystalline, poorly crystalline, and interstratified varieties (127). Distinctions between glauconite and celadonite may be vague in the area of approximately 0.2% tetrahedral Al. Celadonite is found as an alteration mineral in mafic volcanic rocks (127).

**Chlorite and Vermiculite.** Chlorite is a 1.4 nm (14 Å) clay mineral that cannot be expanded or collapsed by traditional laboratory procedures. Chlorite occurs commonly in argillaceous sedimentary rocks and in certain soils. Samples of ocean sediments show that chlorite is most common in the high latitudes (131,132), and that chlorite is also common in sedimentary rocks that have undergone low temperature metamorphism (133) and burial diagenesis (134,135). Chlorite is also commonly found rimming quartz grains, filling pores in sandstones, and replacing grains in limestones (136). In early clay mineral studies chlorite was less well explored than the other clay minerals or the chlorite of igneous and metamorphic occurrences (10,137).

Structurally, the unit layer of chlorite is composed of a 2:1 layer combined with a 0.4 nm Mg or Al interlayer or hydroxide sheet. The 2:1 layer structure has a composition of  $[(\text{R}^{2+}, \text{R}^{3+})_3(\text{Si}_{4-x}\text{R}_x^{3+})\text{O}_{10}(\text{OH})_2]^-$  and the octahedral interlayer has a composition of  $[(\text{R}^{2+}, \text{R}^{3+})_3(\text{OH})_6]^+$ . The tetrahedral cations are typically  $\text{Si}^{4+}$  or  $\text{Al}^{3+}$ , the three-layer (TOT) octahedral cations are typically  $\text{Mg}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Cr}^{3+}$ , and  $\text{Ti}^{4+}$  and the interlayer cations are typically  $\text{Mg}^{2+}$  (brucitelike layer) or  $\text{Al}^{3+}$  (gibbsitelike layer) (37,38,138-140). Clinocllore [12252-52-7],  $\text{Mg}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Mg}_2\text{Al})(\text{OH})_2$ , chamosite [12173-01-2],  $\text{Fe}_3^{2+}(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Fe}_2^{2+}\text{Al})(\text{OH})_2$ , nimite [71618-47-8],  $\text{Ni}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Ni}_2\text{Al})(\text{OH})_2$ , baileychllore [14705-13-4],  $\text{Zn}_3(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Zn}_2\text{Al})(\text{OH})_2$ , donbassite [12415-16-6],  $\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{Al}_2)(\text{OH})_2$ , cookite [1302-92-7],  $\text{Al}_2$



$(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{LiAl}_2)(\text{OH})_2$ , sudoite [12211-44-8],  $\text{Al}_2(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2 \cdot (\text{AlMg}_2)(\text{OH})_2$ , and franklinfurnaceite [110778-47-7],  $\text{Mn}_2^{2+}\text{Mn}_2^{3+}(\text{Zn}_2\text{Si}_2)\text{O}_{10}(\text{OH})_2 \cdot (\text{Ca}_2\text{Mn}^{2+}\text{Fe}^{3+})(\text{OH})_2$ , are also chlorites.

Regularly interstratified (1:1) chlorite and vermiculite has been attributed to the mineral corrensite [12173-14-7] (141). Chlorite mixed layers have been documented with talc, vermiculite, smectite, illite, biotite, kaolinite, serpentine, and muscovite. The mixed-layer mineral is named after the components, eg, talc-chlorite. The earlier literature, however, has reference to specific minerals such as kulkeite [77113-95-2] (talc-chlorite) and tosudite [12424-41-1] (chlorite-dioctahedral smectite) (142).

Aluminum chlorite,  $(\text{Al,Fe})_4(\text{Si,Al})_4\text{O}_{10}(\text{OH})_8$ , in which a gibbsitlike interlayer proxies in part for the brucitelike interlayer, is being discovered in increasing occurrences and abundance (11,141). Chloritelike structures have been synthesized by precipitation of Mg and Al between montmorillonite sheets (143). Cookite [1302-92-7], an aluminous chlorite containing lithium, has been found in high alumina refractory clays and bauxite [1318-16-7] (139).

Vermiculite is an expandable 2:1 mineral like smectite, but vermiculite has a negative charge imbalance of 0.6–0.9 per  $\text{O}_{10}(\text{OH})_2$  compared to smectite which has ca 0.3–0.6 per  $\text{O}_{10}(\text{OH})_2$ . The charge imbalance of vermiculite is satisfied by incorporating cations in two water layers as part of its crystal structure (144). Vermiculite, which can be either trioctahedral or dioctahedral, often forms from alteration of mica and can be viewed as an intermediate between illite and smectite. Also, vermiculite is an end member in a compositional sequence involving chlorite (37). Vermiculite may be viewed as a mica that has lost part of its  $\text{K}^+$ , or a chlorite that has lost its interlayer, and must balance its charge with hydrated cations.

The chemical composition of vermiculite can be quite variable (145). The megascopic varieties are generally trioctahedral, and the clay-size varieties contain both dioctahedral and trioctahedral varieties (144). Smectite minerals do not commonly occur as macroscopic single crystals.

**Palygorskite and Sepiolite.** Palygorskite (attapulgit) and sepiolite are clay minerals in which the 2:1 layers are linked together in chainlike or a combination of chain-sheet structures (12). Because of commercial applications, attapulgit [1337-76-4], named for its occurrence near Attapulgis, Georgia, is a commonly used name for palygorskite. However, it has been determined that the short crystals, called attapulgit, and the longer crystals, palygorskite, have the same crystalline structure (146) and the mineral name palygorskite has precedence (147,148).

Palygorskite and sepiolite are different from other clay minerals in the manner in which the 2:1 layers are joined. Rather than being joined in a continuous manner, the tetrahedral sheets are joined to an adjacent inverted tetrahedral layer, making the octahedral layers noncontinuous and leaving an open channel in the mineral structure (37,38,148). The *b*-dimension of palygorskite is  $\approx 1.8$  nm (18 Å); the *b*-dimension of sepiolite is  $\approx 2.7$  nm (27 Å) (37).

Palygorskite has an ideal formula that approximates  $\text{MgAl}_3\text{Si}_8\text{O}_{20}(\text{OH})_3(\text{OH}_2)_4 \cdot x[\text{R}^{2+}(\text{H}_2\text{O})_4]$ ; the ideal formula for sepiolite is  $\text{Mg}_8\text{Si}_{12}\text{O}_{30}(\text{OH})_4(\text{OH}_2)_4 \cdot x[\text{R}^{2+}(\text{H}_2\text{O})_8]$  (37). The chemical composition of a specific sample may vary widely because there is substitution of Na, Fe, Mn, Al, and Ni in the octahedral



sheet of sepiolite, and substitution of Na, Fe, and Mn in palygorskite (37) giving rise to varieties modified by their substitutional component such as: Mn-sepiolite, Mn-palygorskite, Mn-ferrisepiolite, Mn-ferripalygorskite, (149), falcondoite [62996-88-7], Ni-sepiolite with  $\text{Ni} > \text{Mg}$  (150), Na-sepiolite (loughlinite [22830-49-5]),  $\text{Na}_2\text{Mg}_3\text{Si}_6\text{O}_{16} \cdot 8\text{H}_2\text{O}$  (151), and Al-sepiolite (152).

These clays have distinctive uses and properties not shown by platy clay minerals. The Georgia-Florida deposits originated from evaporating sea water (153). Palygorskites sorb both cations and neutral molecules. Typical cation-exchange capacities are in the order of 20 meq/100 g dry clay. For chemical analysis of attapulgite see Table 4. Sepiolite is used in drilling muds where resistance to flocculation in briny water is desired (see PETROLEUM). Sepiolite and attapulgite are best identified by their 110 reflections, 1.21 and 1.05 nm, respectively, in x-ray powder diffraction (154,155).

**Mixed-Layer Minerals.** In addition to polymorphism resulting from the disordering and proxying of one element for another, clay minerals exhibit ordered and random intercalation sandwiches with one another (12). For example, in mixed-layer clay minerals, sheets of illite may be interspersed with montmorillonite either randomly or regularly (156). Mixed-layer minerals having three components are rare but include illite-chlorite-smectite and illite-smectite-vermiculite (37,157). The accepted names for the identified mixed-layer minerals having components present in fixed percentages are available (158). The concept of how the mineral components are placed in consecutive locations is commonly referred to as Reichweite, or ordering (37,159). A random mixed-layer clay has an ordering of  $R = 0$  (R0) which means that the first mineral (designated A) may be followed by either a second mineral (designated B) or itself, in a random manner. A perfectly ordered mixed-layer that is a 50:50 mixture of two minerals has an ordering of  $R = 1$  (R1) indicating an ABAB order (37). Long-range ABAA order has an order of  $R = 3$  (R3) and is found in illite-smectite and glauconite-smectite mixed-layer minerals (157). The determination of the ordering and the percentage of the mineral components is commonly obtained by x-ray data (37).

Mixed-layer clays, particularly illite-smectite, are very common minerals and illustrate the transitional nature of the 2:1 layered silicates. The transition from smectite to illite occurs when smectite, in the presence of potassium from another mineral such as potassium feldspar, or from thermal fluids, is heated and/or buried. With increasing temperature smectite plus potassium is converted to illite (37,39).

The physical structure of mixed-layer minerals is open to question. In the traditional view, the MacEwan crystallite is a combination of 1.0 nm (10 Å) non-expandable units (illite) that forms as an epitaxial growth on 1.7 nm expandable units (smectite) that yield a coherent diffraction pattern (37). This view is challenged by the fundamental particle hypothesis which is based on the existence of fundamental particles of different thickness (160-162).

The fundamental particle hypothesis assumes that random illite-smectite mixed-layer minerals are actually discrete particles of illite and smectite. During burial diagenesis, or as a response to thermal activity, smectite dissolves and produces fine illite particles. Fine illite crystals stacked upon other fine illite crystals expand upon ethylene-glycol treatment, and can be identified by x-ray techniques as smectite and the entire diffraction package is identified as regular (R1)

illite-smectite. Subsequently, as illite fuses to form thicker particles there are not as many interparticle surfaces to adsorb ethylene-glycol; therefore, the larger crystals appear to be illite-rich illite-smectite mixed-layer minerals (R3). Therefore, in the view of many clay researchers, random illite-smectite may be a physical mixture of discrete illite and smectite particles, whereas regular illite-smectite may be only illite.

An alternative description of illite-smectite mixed-layer clays begins with megacrystals of smectite that incorporate smaller packets of illite (163). These constituents are observed as mixed-layer minerals in x-ray analysis. Diagenesis increases the percentage of illite layer and with increasing alteration the mixed-layer mineral takes on the characteristics of an illite dominated illite-smectite.

Chlorite is another mineral that is commonly associated with mixed-layered clays. Complete solid solutions of chlorite mixed-layer minerals have not been identified. In contrast to illite-smectite mixed-layer minerals, chlorite mixed-layer minerals occur either as nearly equal proportions of end-member minerals (R1) or dominated by one end member (R0) (142). Mixed-layer chlorite may consist of any of the di-tri combinations of chlorite and chlorite mixed-layering occurs with serpentine, kaolinite, talc, vermiculite, smectite, and mica. References of specific chlorite mixed-layer minerals of varied chemical compositions are available (142,156).

### Amorphous and Miscellaneous Groups

**Allophane and Imogolite.** Allophane is an amorphous clay that is essentially an amorphous solid solution of silica, alumina, and water (82). In allophane less than one-half of the aluminum is held in tetrahedral coordinations and the  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  ratio typically varies between 1.3 and 2.0, but values as low as 0.83 have been reported. The typical morphology of allophane is cylindrical (37). Allophane may be associated with halloysite, smectite minerals, or it may occur as a homogeneous mixture with evansite, an amorphous solid solution of phosphorus, alumina, and water. Its composition, hydration, and properties vary. Chemical analyses of two allophane samples are given in Table 5.

The index of refraction of allophane ranges from below 1.470 to over 1.510, with a modal value about 1.485. The lack of characteristic lines given by crystals in x-ray diffraction patterns and the gradual loss of water during heating confirm the amorphous character of allophane. Allophane has been found most abundantly in soils and altered volcanic ash (101,164,165). It usually occurs in spherical form but has also been observed in fibers.

Imogolite [12263-43-3] is an uncommon paracrystalline clay mineral assigned the formula  $1.1 \text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot 2.3-2.8\text{H}_2\text{O}$  (166). All the aluminum is held in octahedral coordination and the  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  ratio typically varies between 1.5-1.15. The morphology of imogolite has been reported as thread-shaped and as hollow spheres. Imogolite is generally viewed as an intermediate between allophane and kaolinite. In modern environments both allophane and imogolite are associated with volcanic material in areas of high rainfall.

**High Alumina Clay Minerals.** Several hydrated alumina minerals should be grouped with the clay minerals because the two types may occur so intimately

Al <sub>2</sub> O <sub>3</sub>	30.41	41.41
Fe <sub>2</sub> O <sub>3</sub>	0.23	0.86
MgO	0.29	0.22
CaO	0.02	0.20
K <sub>2</sub> O + Na <sub>2</sub> O	0.10	0.10
TiO	none	none
CuO	1.60	1.80
ZnO	4.06	4.30
CO <sub>2</sub>	0.65	2.07
P <sub>2</sub> O <sub>5</sub>	0.02	9.23
SO <sub>3</sub>	0.21	0.08
H <sub>2</sub> O removed		
at 105°C	16.38	20.92
above 105°C	14.43	14.43
Total	100.70	99.96

<sup>a</sup>Allophane, Monte Vecchio, Sardinia (82).

<sup>b</sup>Allophane-evansite, Freienstein, Styria (82).

associated as to be almost inseparable. Diaspore ( $\alpha$ -AlO(OH)) and boehmite ( $\gamma$ -AlO(OH)), both Al<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O (Al<sub>2</sub>O<sub>3</sub>, 85%; H<sub>2</sub>O, 15%) are the chief constituents of diaspore clay, which may contain over 75% Al<sub>2</sub>O<sub>3</sub> on the raw basis (27). Gibbsite, Al<sub>2</sub>O<sub>3</sub>·3H<sub>2</sub>O (Al<sub>2</sub>O<sub>3</sub>, 65.4%; H<sub>2</sub>O, 34.6%), and clachite [12197-64-7], the so-called amorphous alumina hydrate (much clachite is probably cryptocrystalline), as well as the monohydrates, occur in bauxite (33,35,167), bauxitic kaolin, and bauxitic clays (168,169).

The hydrated alumina minerals usually occur in oolitic structures (small spherical to ellipsoidal bodies the size of BB shot, about 2 mm in diameter) and also in larger and smaller structures. They impart harshness and resist fusion or fuse with difficulty in sodium carbonate, and may be suspected if the raw clay analyzes at more than 40% Al<sub>2</sub>O<sub>3</sub>. Optical properties are radically different from those of common clay minerals, and x-ray diffraction patterns and differential thermal analysis curves are distinctive.

High alumina minerals are found where intense weathering and leaching has dissolved the silica. It is generally believed that a very humid, subtropical climate is required for this (lateritic) stage of weathering.

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**Table 5. Chemical Analyses of Allophane, wt %**

Component	1 <sup>a</sup>	2 <sup>b</sup>
SiO <sub>2</sub>	22.22	4.24

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T. DOMBROWSKI

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**USES**

Clays are composed of extremely fine particles of clay minerals which are layer-type aluminum silicates containing structural hydroxyl groups. In some clays, iron or magnesium substitutes for aluminum in the lattice, and alkalies and alkaline earths may be essential constituents in others. Clays may also contain varying amounts of nonclay minerals such as quartz [14808-60-7], calcite [13397-26-7], feldspar [68476-25-5], and pyrite [1309-36-0]. Clay particles generally give well-defined x-ray diffraction patterns from which the mineral composition can readily be determined.

Clay particles are so finely divided that clay properties are often controlled by the surface properties of the minerals rather than by bulk chemical composition. Particle size, size distribution, and shape; the nature and amount of both mineral and organic impurities; soluble materials, nature, and amount of exchangeable ions; and degree of crystal perfection are all known to affect the properties of clays profoundly.

Clays are classified into six groups by the U.S. Bureau of Mines (1): kaolin, ball clay, fire clay, bentonite, fuller's earth, and common clay and shale. About half the tonnage of clays produced in the United States is in the last category. In terms of monetary value, however, kaolin accounts for about two-thirds of the dollar volume.

**Ceramic Products**

A large proportion of the annual production of ball clay, fire clay, and common clay and shale are used for ceramics (qv). Ceramic products are generally considered to be products made from fine-grained oxides, silicates, and many other naturally occurring materials through the application of high temperature. The

resulting fired products may be polycrystalline, as are whiteware, bricks, etc, or a vitreous glassy material, eg, glass (qv), or combinations of both types of materials, such as porcelain enamel (see ENAMELS, VITREOUS OR PORCELAIN). Increasingly ceramics are being produced from synthetic materials of high purity because of the unique properties that may be obtained (see ADVANCED CERAMICS). The clays used in conventional ceramics are far from being pure compounds.

In general, ceramic ware is produced by plasticizing the clay by the addition of water so that it may be shaped or formed into the desired object. Ceramic products may also be formed by dispersing the clay in water to form a slip which is then cast in a plaster mold. After being shaped, the object is dried to increase its strength so that it may be handled, and is then fired at elevated temperatures until there has been some vitrification or fusion of the components to form a glassy bond that makes the shape permanent and strong so that the object does not disintegrate in water. In the case of porcelain enamel the slip is sprayed on a metal surface and then fired.

**Properties.** *Plasticity.* Plasticity may be defined as the property of a material that permits it to be deformed under stress without rupturing and to retain the shape produced after the stress is removed. When water is added to dry clay in successive increments, the clay becomes workable, that is, readily shaped without rupturing. The workability and retention of shape develop within a very narrow moisture range.

Plasticity may be measured by determination of: (1) the water of plasticity defined as the amount of water necessary to develop maximum plasticity, a subjective judgment, or the range of water content in which plasticity is demonstrated; (2) the amount of penetration of an object, frequently a needle or some type of plunger, into a plastic mass of clay under a given load or rate of loading and at varying moisture contents; and (3) the stress necessary to deform the clay and the maximum deformation the clay undergoes before rupture at different moisture contents and with varying rates of stress application.

In ceramics, plasticity is usually evaluated by means of the water of plasticity. Values for the common clay minerals are given in Table 1. Each clay mineral can be expected to show a range of values because particle size, exchangeable ion composition, and crystallinity of the clay mineral also exert an influence. Nonclay mineral components, soluble salts, organic compounds, and texture can also affect the water of plasticity.

In general, a relatively low value for water of plasticity is desired in ceramics and hence kaolinite, illite, and chlorite [14998-27-7] clays have better plasticity characteristics than attapulgite or montmorillonite. The plasticity values of the first group are changed only slightly by variations in the exchangeable cation composition. However, sodium gives lower values than calcium, magnesium, potassium, and hydrogen. In the case of montmorillonite, the water of plasticity varies considerably with the nature of the exchangeable cations, sodium giving higher values than the others.

Clays composed only of clay minerals may have higher water of plasticity values than desired. Consequently, the presence of substantial amounts of nonclay minerals or the addition of materials that reduce the water of plasticity may improve the working characteristics of a clay.

**Table 1. Ceramic Properties of Clay Minerals**

Property	Mineral				
	Kaolinite	Illite	Halloysite	Montmorillonite	Attapulgite
CAS Registry Number	[1318-74-7]	[12173-60-3]	[12244-16-5]	[1318-93-0]	[1337-76-4]
water of plasticity, % <sup>a</sup>	8.9-56.3	17-38.5	33-50	83-250	93
strength, kg/cm <sup>2</sup>					
green <sup>b</sup>	0.34-3.2	3.2	5	5 <sup>c</sup>	
dry <sup>a</sup>	69-4840	1490-7420	1965	1896-5723	4482
linear shrinkage, % <sup>a</sup>					
drying <sup>d</sup>	3-10	4-11	7-15	12-23	15
firing <sup>e</sup>	2-17	9-15	20	11	23

<sup>a</sup>Ref. 2.<sup>b</sup>Ref. 3.<sup>c</sup>Calcium montmorillonite.<sup>d</sup>Percentage of dry length: 5 h at 105°C.<sup>e</sup>Allophane [12172-71-3] has a linear shrinkage value for firing of 50%.

Plasticity in clay-water systems is caused by a bonding force between the particles and water which acts as a lubricant and permits some movement between the particles under the application of a deforming force. The bonding force is in part a result of the charges on the particles (see CLAYS, SURVEY).

**Green Strength.** Green strength is the transverse breaking strength measured while the plasticizing water is still present. As water is continuously added to a dry clay, strength increases to a maximum and then decreases. The strength at water of plasticity is, in general, lower than the maximum strength. Values for the common clay minerals are given in Table 1.

As in the case of plasticity, green strength values would be expected to vary with exchangeable cation composition to only a slight degree for kaolinite, illite, and chlorite, and to a considerable degree for montmorillonite. In the last, sodium would be expected to provide higher maximum green strength than other common cations. Poorly crystallized varieties of kaolinite and illite yield higher green strength than well-crystallized varieties. The presence of large quantities of non-clay minerals reduces the green strength, whereas small amounts may actually increase the strength because these permit the development of a more uniform clay body. Green strength is also related to the particle size such that smaller particles provide higher strength. If the clay mineral particles develop preferred orientation in certain directions during formation of the ware, the breaking strength is somewhat greater in the transverse direction to the preferred orientation.

**Drying Properties. Drying Shrinkage.** The reduction in length or volume that takes place on drying is termed drying shrinkage. As a rule, drying shrinkage increases as the water of plasticity increases and, for a particular clay mineral, it increases as the particle size decreases. In addition, drying shrinkage varies with the degree of crystallinity. Ball clay, which contains relatively poorly ordered kaolinite, shows values at the high end of the range of typical values shown in

Table 1. The nature of the adsorbed cation causes variations in the amount of drying shrinkage only as it affects the water of plasticity.

The presence of nonclay minerals tends to reduce drying shrinkage depending on mineral shape, particle size distribution, and abundance. Granular particles having a wide distribution of sizes are most effective. The presence of nonclay minerals at about 25% of the ceramic body composition is generally desirable for minimizing shrinkage. Drying shrinkage is also related to texture. For example, if the clay mass shows parallel orientation of the basal plane surfaces of the clay minerals, shrinkage in the direction at right angles to the basal planes is substantially greater than in the direction parallel to them (4).

In the initial drying phase of a clay body the volume shrinkage is about equal to the volume of water evaporated. Beyond a given moisture content there is either no further shrinkage or only a very small amount of water is lost. The water lost during the shrinkage interval is called shrinkage water and is that which separates the component particles. The critical point at which shrinkage stops is reached when the moisture film around the particle becomes so thin that the particles touch one another and shrinkage can go no further. The water loss following the shrinkage period is called pore water.

In the production of ceramic ware the shape of the ware must be retained after drying and the ware must be free from cracks and other defects. Controlled drying helps to minimize defects. In general, clays containing moderate amounts of nonclay minerals are easier to dry than those composed wholly of clay minerals. Furthermore, clays composed of illite, chlorite, and kaolinite are relatively easier to dry than those composed of montmorillonite.

**Dry Strength.** Dry strength is measured as the transverse breaking strength of a test piece after drying long enough, usually at 105°C, to remove almost all the pore and adsorbed water. Values, given in Table 1, usually show a large range because of variations in particle size distribution, crystallinity, and, especially for montmorillonite, the nature of the exchangeable ions.

Large amounts of nonclay mineral components, especially if the particles are well sorted, tend to reduce the dry strength. In general, the dry strength is higher when sodium is the adsorbed cation. The presence of organic matter in some clays increases dry strength and this appears partly to be the explanation for the high dry strength for some ball clays. A principal factor in determining dry strength is the particle size of the clay mineral component. The maximum strength increases rapidly as the particle size decreases.

**Firing Properties.** Heating clay materials to a sufficiently high temperature results in fusion of the material. In the 100–150°C range, the shrinkage and pore water are lost with the attendant dimensional changes. In general, the rate of oxidation increases with increasing temperature. The oxidation of sulfides, present in many clays, frequently in the form of pyrite,  $\text{FeS}_2$ , begins between 400 and 500°C. Beginning at about 500°C and in some cases continuing to 900°C, the hydroxyl groups of the clay minerals condense and are driven off as water vapor. The exact temperature, rate, and abruptness of the loss of hydroxyls depend on the nature of the clay minerals and the particle sizes. Reduction of particle size, particularly if accompanied by poor crystallinity, tends to reduce the temperature interval. Kaolinite and halloysite minerals lose hydroxyls abruptly at 450–600°C. The loss of hydroxyls from montmorillonite minerals varies greatly with structure

and composition but is generally slower and more gradual than that for kaolinite and halloysite.

The loss of hydroxyls is usually accompanied by a modification, not a complete destruction of the structure. In the montmorillonite-type clay minerals, hydroxyl loss is not accompanied by shrinkage, whereas in kaolinite and halloysite the loss is accompanied by shrinkage, which continues up into the vitrification range. In the range of 800 to 900°C, the structure of the clay mineral is destroyed and significant firing shrinkage develops. Values for firing shrinkage are also given in Table 1. The range of shrinkage values results from variations in size and shape of the clay mineral particles, the degree of crystallinity, and in the case of the montmorillonite-type of minerals, variations in composition.

At temperatures above about 900°C new crystalline phases develop from all the clay minerals except those containing large amounts of iron, alkalies, or alkaline earths. In these latter cases fusion may result after the loss of structure without any intervening crystalline phase. Frequently there is a series of new high temperature phases developing in an overlapping sequence as the mineral is heated to successively higher temperatures. This is followed by complete fusion of the mineral, which, in the case of kaolinite, takes place at 1650–1775°C. For the montmorillonite-type minerals, the fusion temperature varies from about 1000 to 1550°C, the lower values being found in minerals relatively rich in iron, alkalies, and alkaline earths.

The initial high temperature phases are frequently related to the structure of the original clay mineral, whereas the later phases developing at higher temperatures are related to the overall composition. In the development of high temperature phases, nucleation of the new lattice configuration takes place first, followed by a gradual growth of the new structure and an increase in its perfection as the temperature is raised. Traces of various elements cause substantial changes in the temperature and the rate of formation of the high temperature phases.

**Miscellaneous.** Other important properties are resistance to thermal shock, attack by slag, and, in the case of refractories (qv), thermal expansion. For white-ware, translucency, acceptance of glazes, etc, may be extremely important. These properties depend on the clay mineral composition, the method of manufacture and impurity content.

**Raw Materials.** Raw material requirements vary widely, depending on use.

**Brick.** Almost any clay composition is satisfactory for the manufacture of brick unless the clay contains a large percentage of coarse material that cannot be eliminated or ground to adequate fineness. A high concentration of nonclay material in a silt-size range may cause difficulties by greatly reducing the green and firing strength of the brick. Montmorillonite should be absent, or present only in very small amounts, or the shrinkage may be excessive. Clays composed of mixtures of clay minerals having from 20–50% of unsorted fine-grain nonclay materials are most satisfactory. Large amounts of iron, alkalies, and alkaline earths, either in the clay minerals or as other constituents, cause too much shrinkage and greatly reduce the vitrification range; thus, a clay with a substantial amount of calcareous material is not desirable. Face bricks, which are of superior quality, are made from similar materials but it is even more desirable to avoid these detrimental components (see BUILDING MATERIALS, SURVEY).

**Tile.** Roofing and structural tiles are usually made from the same material as face brick. Drain tiles have a high porosity, which is frequently obtained by firing at a low temperature. Drain tiles are often made from clays having about 75% of fine-grained nonclay mineral material in addition to components that provide a high green and dry strength and a low fusion point. Wall and floor tiles are frequently made of mixtures where talc and kaolin are the primary components.

**Terra-Cotta, Stoneware, Sewer Pipe, and Paving Brick.** Clays composed of mixtures of clay minerals containing 25–50% fine-grained unsorted quartz are well suited for the manufacture of terra-cotta, stoneware, sewer pipe, and paving brick. A small amount of montmorillonite can be tolerated, but a large amount gives undesirable shrinkage and drying properties. In general, clays having low shrinkage, good plastic properties, and a long vitrification range should be used.

**Whiteware.** Porcelain and dinnerware are made up of about equal amounts of kaolin, ball clay, flint (ground quartz), feldspar, or some other white-burning fluxing material such as talc [14807-96-6] and nepheline. The kaolin clay is composed of well-crystallized particles of kaolinite. Ball clays are white-burning, highly plastic, and easily dispersible. They provide the plasticity necessary in the forming of the ware and adequate green and dry strength for handling. The chief component of most ball clays is extremely fine-grained and poorly organized kaolinite. However, some ball clays are known, for example, those in south Devonshire in Great Britain, that contain remarkably well-ordered kaolinite. Some ball clays also contain small amounts of illite and/or small amounts of montmorillonite which may add to desired properties. Many ball clays also contain a small but significant amount of organic material that also appears to enhance the desired properties. Small amounts of bentonites and, in some cases, halloysite, are also used in whiteware bodies as replacements of ball clay to increase dry strength.

**Porcelain Enamel.** The slurry used in enameling is commonly composed of ball clay, frits, and coloring pigments (qv). The frits are finely ground particles of glass with a low fusion temperature.

**Refractories.** Refractory products are prepared from a wide variety of naturally occurring materials such as chromite [1308-31-2] and magnesite [546-93-0] or from clays predominantly composed of kaolinite. Increasingly, higher purity synthetic materials are being used to obtain special properties. On the other hand, for many refractory uses, a somewhat lower fusion point than that provided by kaolinite may be adequate, so that clay materials having a moderate amount of other components as, for example, illite, may be satisfactory. High alumina clays are also used extensively for the manufacture of special types of refractories.

An interesting type of clay used widely in the manufacture of refractories is so-called flint clay, which is very hard and has very slight plasticity even when finely ground. Flint clays are essentially pure, extremely fine-grained kaolinite. In some cases the hardness appears to result from the presence of a small amount of free silica acting as a cement, whereas in other cases it is the result of an intergrowth of extremely small kaolinite particles.

## Paper

The paper (qv) industry is the largest consumer of processed clays, nearly all of which is kaolin (5,6). Kaolin has two main uses in paper: as a filler where kaolin

is mixed with pulp (qv) fibers (see **FILLERS**); and as a coating where kaolin is combined with water, binders, and various additives and coated onto the surface of the paper sheet (see **PAPERMAKING MATERIALS AND ADDITIVES**). Its widespread use results from the fine particle size, chemical inertness, insolubility over a wide range of pH, white or nearly white color, and low cost. As a filler, kaolin improves opacity of the sheet, imparts smoothness to the surface, and replaces some of the more expensive pulp fibers. In coatings (qv) the kaolin imparts opacity, brightness, a glossy finish, and greatly improved printing quality over that of the uncoated sheet.

**Types of Kaolin.** Kaolins for use in paper are generally classified into three groups according to processing: air-floated, water-washed, or calcined. Kaolins that are air-floated are processed by selecting appropriate crudes, drying, crushing, and pulverizing. In some cases oversize particles are removed by air classification. Some air-floated clays may be slurried in water at 70% solids for convenience in handling and shipping. The addition of a deflocculating agent is required in order to obtain a low viscosity.

Water-washed kaolins are of higher added value than air-floated clays because the more elaborate processing that they receive gives more uniform products. Wet processing of kaolin consists of mining selected crudes, dispersing in water, degritting to remove oversize particles (screening, sedimentation, cyclones), centrifugal fractionation into different size fractions, chemical bleaching (oxidative, reductive or both), filtration, redispersion, and drying. Many variations of this scheme are used to obtain kaolin products having different properties. High intensity magnetic separation of weakly magnetic impurities (see **SEPARATIONS, MAGNETIC**), froth flotation (qv), and selective flocculation are used to remove colored impurities and improve product brightness. Delamination, a selective grinding process that gives platelike particles of high aspect ratio, may also be used to give products that provide improved opacity and print quality (7). Figure 1 gives a general outline of wet processing of kaolin.

Following wet processing, fine particle size kaolins may be calcined, ie, heat treated at about 1000°C. This treatment converts the kaolin to an amorphous pigment of significantly higher brightness and opacity (8). Properties of the various types of kaolins used in paper are shown in Table 2.

**Sources.** The largest sources of kaolin for the paper industry are Cornwall in southwestern England and the middle Georgia area in the United States. Smaller, but important, sources of production are located in Australia and Brazil. Many other sources of kaolins for paper are located in various countries but production is small and frequently the product characteristics are such that use is limited to filler applications. Kaolins from each area have different characteristics that can be traced to the geologic origin of the crude material (9). For example, English kaolins tend to be coarser and slightly whiter than standard brightness United States kaolins, whereas commercially produced Australian and Brazilian kaolins are very fine in particle size.

**Properties.** The properties of kaolin that make it useful in the paper industry are brightness, viscosity, and particle size and shape.

Paper is usually white, thus it is important that materials used in making it are also white. Brightness, the percent reflectance of blue light, is the commonly used measure of kaolin whiteness. Higher brightness is usually more desirable, thus brighter kaolins command higher prices. Water-washed kaolins are gener-



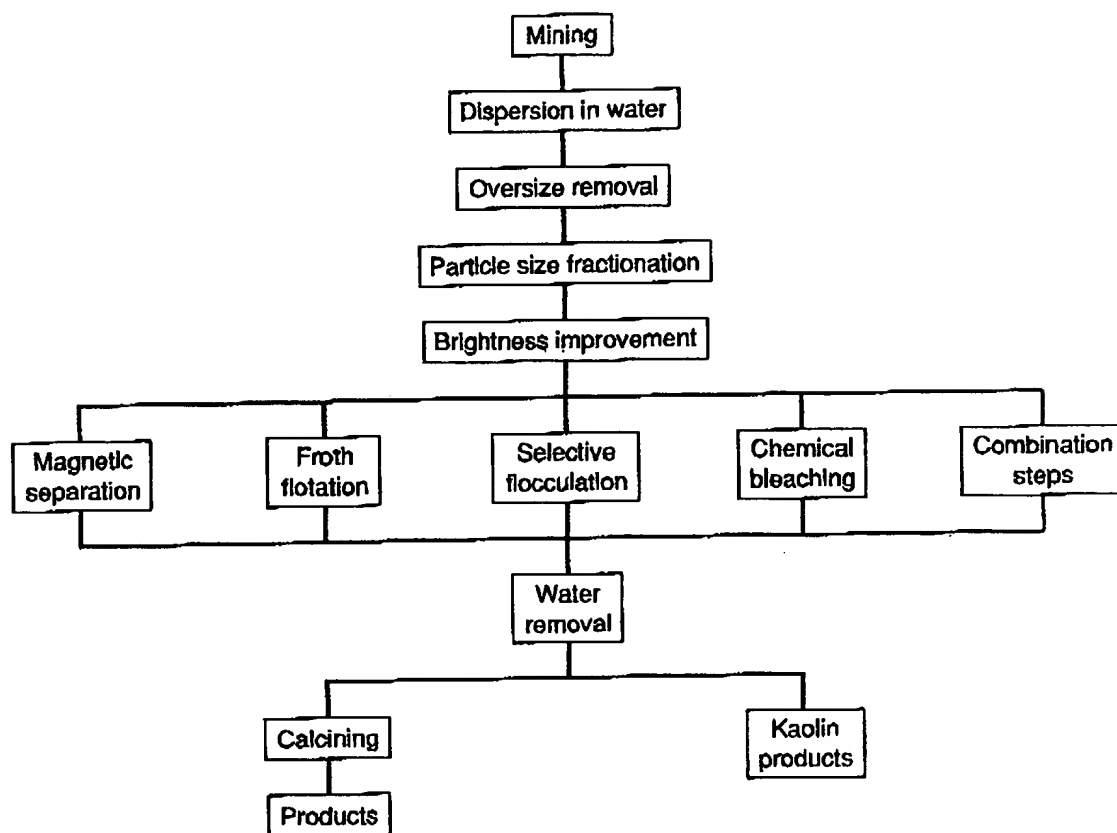


Fig. 1. Schematic for the wet processing of kaolin.

ally higher in brightness and of more uniform color than the air-floated products. Calcined products are of still higher brightness.

For paper coating applications it is desirable that kaolins give fluid aqueous slurries at high (typically 70%) solids, because coating is carried out at high solids to minimize costly drying on the paper machine. A considerable amount of kaolin is shipped as a slurry for convenience in handling so that higher solids gives lower shipping costs. Except when shipped as a slurry, low viscosity at high solids is less important in filler applications because the clays are mixed with pulp fibers in a dilute suspension.

Particle size or particle size distribution is important because properties of the kaolin pigments are very dependent on the size of the individual particles. In general, in paper coatings, finer particle size kaolins give higher brightness, better opacity, and higher gloss to the finished sheet. All coating kaolins must be virtually free of oversize particles, generally defined as 44  $\mu\text{m}$  (325 mesh) sieve residue. These larger pieces cause scratches on the paper in high speed coating operations and give visible imperfections in the sheet surface.

The finer particle fractions of kaolin are typically small platelets having a roughly hexagonal shape. The platy nature of the particles is one of the characteristics of kaolin that makes it so valuable as a paper coating pigment because in the coating operation the particles orient themselves parallel to the fiber substrate to give the desired smooth surface. The coarser particles, at least from the middle Georgia deposits, consist of stacks of loosely bound platelets, commonly



**Table 2. Kaolin Grades for the Paper Industry**

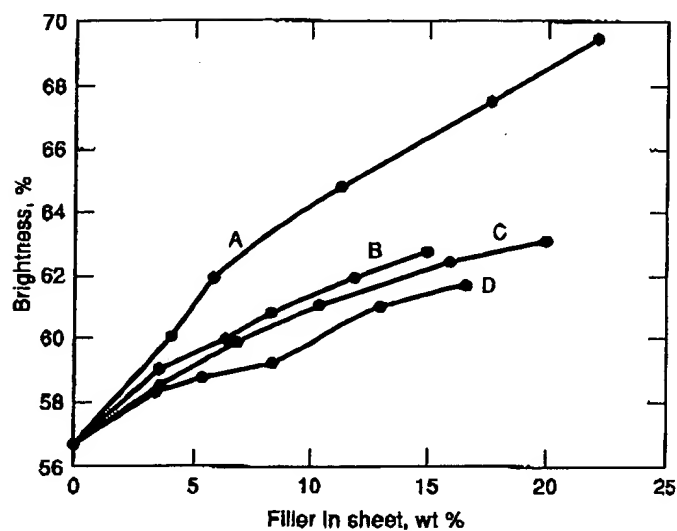
Kaolin type <sup>a</sup>	Brightness, %	Maximum solids, %	Median particle size, $\mu\text{m}$	Uses	Relative cost <sup>b</sup>
<i>Air-floated</i>					
	81-85	<sup>c</sup>	0.30-0.35	filling	L
<i>Water-washed</i>					
standard brightness					
coarse particle (no. 3)	82-85	<sup>c</sup>	1.0-2.0	filling	L-M
intermediate (no. 2)	86	70	0.40-0.55	filling, coating	M
fine (no. 1)	87	70	0.30-0.40	coating	M
ultrafine (ultrafine no. 1)	87	70	0.25-0.30	high gloss coating	M
high brightness					
intermediate	90	70	0.40-0.55	filling, coating	M-H
fine	90	70	0.30-0.40	coating	M-H
ultrafine	90	70	0.25-0.30	high gloss coating	M-H
<i>Calcined</i>					
	93	50 <sup>c</sup>	0.70	filling, coating	Ht

<sup>a</sup>Usual paper-grade designation is given in parentheses.<sup>b</sup>L = low; M = moderate; H = high; Ht = highest.<sup>c</sup>Filler applications do not require low viscosity at high solids.

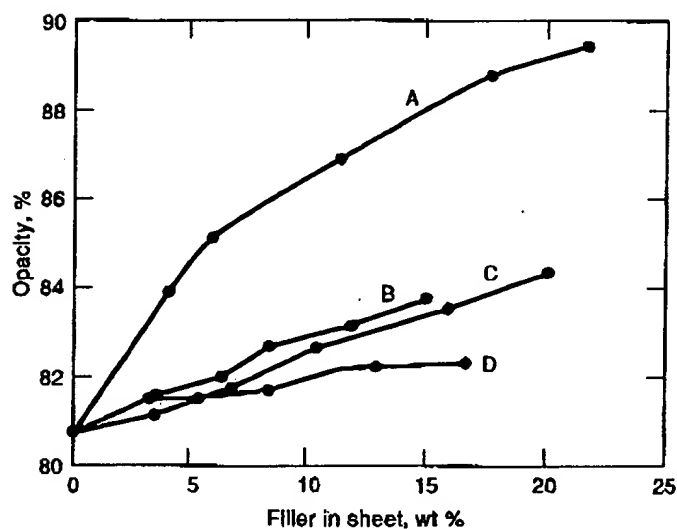
described as booklets (10). These can be selectively ground to give delaminated kaolin products of quite different characteristics than those of the naturally occurring material (11). The larger diameter but thin platelets that are obtained by delamination are especially valuable in obtaining good coated paper quality even at very light coating weights. Delamination also improves brightness because the resulting particles are better light scatterers and do a better job at obscuring discolored impurities. When used as filler pigments, the large diameter platey delaminated particles are retained well in the sheet and improve its optical properties.

**Filling.** Changes in paper sheet brightness and opacity resulting from addition of various levels of some kaolin clay products are given in Figure 2. It is evident that the improvements in both brightness and opacity are greatest for the fine-particle calcined kaolin. All of the uncalcined kaolins give a lesser brightness and opacity improvement.

**Coating.** Table 3 shows how coated paper properties change with particle size. As a general rule, finer particle kaolins give improved gloss, opacity, and brightness. For extremely fine kaolins, however, opacity and brightness may decrease as a result of the loss of light scattering power of the very fine fractions and an increase in colored impurities.



(a)



(b)

**Fig. 2.** (a) Brightness improvement obtained by the use of kaolin as a filler in paper and (b), opacity improvement obtained as pulp fibers are replaced with various kaolins. In both cases, A represents fine-particle calcined clay; B, high brightness No. 1 kaolin; C, coarse-particle water-washed kaolin; and D, air-floated kaolin.

**Table 3.** Effect of Particle Size on Coated Sheet Properties

Particle size		Coated sheet properties		
% < 2 $\mu\text{m}$	Median, $\mu\text{m}$	Gloss	Brightness, %	Opacity, %
35	3.80	25	71.6	84.2
54	1.80	31	72.2	84.6
78	0.75	33	72.6	84.6
85	0.68	39	72.7	84.7
96	0.46	45	72.6	84.7

**Testing.** The Technical Association of the Pulp and Paper Industry (TAPPI) gives test methods that are widely used by kaolin suppliers to the paper industry. These include tests for viscosity, viscosity stability, brightness, pH, particle size distribution, moisture content, and screen residue (12). Other tests on kaolins that relate to use properties are carried out by kaolin suppliers.

### Molding Sands

Molding sands, composed essentially of sand and clay, are used extensively in the metallurgical industry for the shaping of metal by the casting process (see METALLURGY). Using a pattern, a cavity of the desired shape is formed in the sand into which molten metal is poured and then allowed to cool.

The molding sand may be a natural sand containing clay or a synthetically prepared mixture of clean quartz sand and clay. Synthetic sands are widely used because they can be prepared to meet property specifications and properties are more easily controlled when used. A small amount of water must be added to the molding sand to impart plasticity to develop cohesive strength so that the sand can be molded around the pattern, and to give the sand sufficient strength to maintain the cavity after the pattern is removed and while the metal is poured into it. These properties vary greatly with the amount of tempering water as well as the nature of the clay.

In foundry practice the same sand is used repeatedly. Because the high temperature of the metal dehydrates and vitrifies some of the clay, fresh clay must be added continuously as the sand is used. The only completely adequate test for the satisfactory use of a clay in bonding molding sands is the result obtained by actual use in foundry practice.

**Raw Materials.** The bentonites, composed essentially of montmorillonite and used extensively in bonding molding sands, are of two types. The type carrying sodium as a principal exchangeable cation is produced largely in Wyoming. The calcium carrying type is produced in Mississippi and in many countries outside the United States, such as England, Germany, Switzerland, Italy, the former USSR, South Africa, India, and Japan. Natural calcium montmorillonites are occasionally treated with various sodium compounds so that the properties are similar to the naturally occurring sodium bentonites of Wyoming.

Plastic clays composed largely of poorly crystallized kaolinite but having small amounts of illite, and at times montmorillonite, are widely used in bonding molding sands, especially in the United States.

A third type of clay used in foundries is composed essentially of illite. Most illite clays have a bonding strength and plasticity too low for bonding use, but there are some varieties that have properties approaching those of montmorillonite. The illite in such clays is fine-grained, poorly organized, and frequently associated with mixed layer assemblages containing montmorillonite. Illite bonding clays are produced extensively in Illinois.

**Properties.** The value of a clay for bonding molding sand is usually determined by the green and dry compression strengths of mixtures with varying amounts of the clay and to which varying amounts of tempering water have been added. Other properties such as the bulk density, flowability, permeability, and

hot strength may be important. Standard procedures for determining the properties of bonding clays have been published (13).

Green compression strengths in the range from about 35 to 75 kPa (5–11 psi) are desired in actual practice. Green compression strength is highly dependent on the amount of clay present as well as its type. Typically calcium montmorillonite gives the highest green compression strength, whereas kaolinite and illite have about the same strength but considerably lower values. Sodium montmorillonite and halloysite give a value intermediate between these two extremes (14).

### Plastics and Rubber

Clays used in plastics and rubber have historically been divided into two categories: fillers that extend a polymer or fillers that reinforce a polymer. Extenders are generally classified as such because they are low in cost compared to the polymer into which they are incorporated. A preferred term for clays used as extenders might be functional fillers because addition to a polymer almost always alters its properties to some extent (15).

Kaolin is by far the primary clay mineral filler used in polymers and various grades are produced by several manufacturers specifically for use in this industry. Table 4 lists the most important kaolin grades used as components in plastics and rubber. More than half the tonnage in polymer applications is accounted for by air-floated kaolin, primarily because of its extensive use in rubber. Attapulgite is used for some applications. The use of attapulgite as a replacement for asbestos (qv) in phenolic-based brake linings is increasing (see BRAKE LININGS AND CLUTCH FACINGS).

**Table 4. Kaolin Grades for Polymer Applications**

Kaolin type	Brightness, %	Median particle size, $\mu\text{m}$	Uses	Relative cost <sup>a</sup>
<i>Air-floated</i>				
regular	73–76	0.2–1.0	rubber	L
surface treated	73–76	0.2–1.0	rubber	M
<i>Water-washed</i>				
coarse particle	79–82	4.8	thermosets	M
intermediate	85–87	0.6	PVC	M
fine	86–88	0.4	PVC	M
<i>Calcined</i>				
meta kaolin	84–86	1.4	PVC insulation	H
high temperature	90–92	1.4	engineering plastics, PVC	H
surface treated	90–92	1.4	engineering plastics, PVC	Ht

<sup>a</sup>L = low; M = moderate; H = high; Ht = highest.

**Types of Kaolin.** As can be seen from Table 4, kaolins for use in polymers may be subdivided into the categories of air-floated, water-washed, and calcined. The processing of each of these types is similar to that for use in the paper industry.

The calcined or meta kaolin is used almost exclusively in poly(vinyl chloride) wire insulation because it enhances the electrical resistivity of the compound.

An important group of clays used in polymers are those labeled "surface treated" in Table 4. These products are made from a fully calcined kaolin, an air-floated kaolin, or a water-washed kaolin. Several types of chemical compounds are used to convert the somewhat hydrophilic surface into a more oleophilic surface that is more compatible with polymers (15). Of special utility are calcined kaolins that have been treated with silanes. Although silane treatment raises the cost of kaolin-based fillers significantly, the improvement in polymer properties justifies the extra cost. The data of Table 5, for example, show the effect on physical properties of adding 40% of an aminosilane-treated high temperature calcined kaolin to a nylon compound. The improvement in strength properties and the marked increase in heat deflection temperature are noteworthy. Custom processors can treat clay minerals using a wide variety of materials to alter surface properties.

**Sources.** Kaolin for use in polymers is obtained from the same sources as those for paper clays. Attapulgite is obtained from producers in southern Georgia and northwest Florida.

**Properties.** Properties of clays that make them useful in the plastics and rubber industries are color, particle size and shape, and viscosity. Except for applications in black compounds, clays used in the polymers industry are required to be white or nearly so. Because the refractive index of clays quite closely matches that of most polymer compounds, clays contribute little to opacity and color. In many cases the color of the compound is detrimentally affected by clays because high refractive index iron and titanium impurities become more visible. Frequently a titanium dioxide [13463-67-7] pigment is used along with the clay because the high refractive index gives good opacity and obscures any discoloring materials present in the clay.

Particle size and shape are important because large particles may give a rougher than desired surface whereas small particles are more effective in

**Table 5. Effect of Clay Filler on Nylon Properties<sup>a</sup>**

Property	Unfilled	Filled
tensile strength, MPa <sup>b</sup>	82	97
tensile elongation, %	60	8
tensile modulus, MPa <sup>b</sup>	2900	6200
flexural strength, MPa <sup>b</sup>	97	159
flexural modulus, MPa <sup>b</sup>	2900	6200
izod impact, J/m	0.020	0.017
deflection temp. at 1.82 MPa, °C	77	204

<sup>a</sup>Data for 40% loading of aminosilane-treated calcined kaolin in nylon-6,6.

<sup>b</sup>To convert MPa to psi, multiply by 145.

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increasing the polymer hardness. Particles having a high aspect ratio, ie, "platey" particles, can give greater reinforcement than more isometric particles.

The incorporation of a clay filler into a polymer may strongly affect the viscosity of the compound, especially when finer clays are used. In general, finer particle clays increase viscosity more than coarser particle ones. Depending on the polymer and its application, increasing the viscosity may be desirable or undesirable. For example, a polymer that is too fluid to handle by some processing equipment may be rendered sufficiently viscous to be utilized by the incorporation of a clay filler. Surface treated clays, because of the more oleophilic surface, give lower viscosity compounds than do untreated counterparts.

**Testing.** Various test methods are provided by ASTM (16). These include pigment tests of importance such as chemical analysis, presence of oversize particles, oil absorption, particle size distribution, degree of dispersion, presence of soluble components, etc. Numerous tests are also given by ASTM for the properties of filled and unfilled polymers. These include, for example, such properties as impact resistance, stiffness, viscosity, tear resistance, hardness, color, and electrical resistivity.

**Drilling Fluids**

In oil well drilling a fluid is pumped down the well through a hollow drill string and through nozzles in the bit in the bottom. The fluid returns to the surface through the annulus between the drill string and the wall of the bore. This fluid is usually water-based although oil-based fluids are sometimes used. The use of a drilling fluid has several purposes: it cools and lubricates the drill string, it suspends the cuttings removed by the bit, its density helps to suspend the drill string, and it keeps out formation fluids. Once the drilling fluid reaches the surface, cuttings are removed and the fluid is recycled down the bore (see PETROLEUM, DRILLING FLUIDS AND OTHER OIL RECOVERY CHEMICALS).

Clays are an important ingredient in most water-based drilling fluids. Specifically montmorillonite (in the form of bentonite), attapulgite, and sepiolite [15501-74-3] are used. The primary function is to control viscosity and the suspension properties of the fluid. In a drilling fluid, non-Newtonian viscosity is desired. At the high shear rates encountered at the drill bit, the fluid should be of low viscosity yet under lower shear rates it should be sufficiently viscous to suspend the cuttings removed. Under static conditions it should give sufficient gel strength to prevent settling of the cuttings. Clays are not usually used as the sole viscosity control agent and typically organic water-soluble polymers (qv) such as starch [9005-225-8] (qv), carboxymethylcellulose (CMC) [9004-32-4], natural gums, or synthetic organic polymers are used in conjunction with them. These polymers also aid the clay component of the drilling mud to serve as a filtration aid, ie, prevent the drilling fluid in the bore hole from being lost into the formation.

In addition to clays, weighting agents are added to increase the drilling fluid density so as to prevent blowouts from high pressure in the formation. Dispersants (qv) are added to control viscosity. Weighting agents are usually finely ground natural minerals of high density such as barite [13462-86-7] or hematite [1317-60-8]. Dispersants used are those commonly used for deflocculating clay

such as tetrasodium pyrophosphate [7722-88-5], sodium hexamethaphosphate [10124-56-8], and lignin sulfonates [8061-51-6].

Bentonite is the principal clay used in drilling fluids and most domestic production is in the Wyoming-Montana-South Dakota area. This bentonite is largely in the sodium form and gives the desired high viscosity at low concentrations. Attapulgite from northern Florida and southern Georgia is preferred in those cases where saltwater is used in the drilling fluid or encountered in the borehole. Attapulgite, although more costly than bentonite, maintains its high viscosity better than bentonite in the presence of flocculating salts (17). Sepiolite is used where the highest temperature stability is needed. Bentonite that has been treated to render it oleophilic is used in oil-based muds. Test methods for clay properties of value in drilling fluids are provided by the American Petroleum Institute (18).

### Paint

Clays are widely used in both oil-based and water-based paints (see PAINT). In this application, clays perform several important functions: they extend the much higher cost titanium dioxide opacifying pigment, control viscosity so as to prevent pigments from settling during storage, provide thixotropy so that the paint is easily applied yet does not sag after application, improve gloss retention, promote film integrity, and aid in tint retention.

Kaolins for use in paints are similar to those used in both plastics and paper but are processed somewhat differently so as to enhance the properties of the paint. Both calcined and uncalcined kaolins are used. Calcined kaolins are of higher cost than uncalcined kaolin, but considerably less costly than titanium dioxide. The calcined kaolins contribute significantly to opacity so that they can be used to replace part of the  $\text{TiO}_2$  with no loss of hiding power. Although kaolins are easily wetted by both oil and water, surface treatment may sometimes be used to enhance the oleophilic properties. The kaolin in paint may represent 20-30% of the pigment.

Bentonite and attapulgite are also used but as a viscosity control and suspending agent rather than as an extender pigment because their very fine particle size contributes little to opacity. Bentonites and attapulgites for paint use must be processed to remove oversize particles. Organic treated bentonites are widely used as suspending and antisag agents in oil-based paints. Whiter grades are preferable so as to contribute as little as possible to the color of the finished paint. Procedures for paint raw materials and finished paint are available (16).

### Miscellaneous

Clays are used in a vast number of products. In a few cases, clays are used as a chemical raw material as, for example, for synthetic zeolite production or for production of aluminum.

**Adsorbents.** Acid activated clays have been widely used to treat mineral, vegetable, and animal oils (see VEGETABLE OILS). The primary objective of such

treatment is decolorization and, at least in the case of edible oil, to remove components that contribute to off-tastes. Typically the oil is filtered through a granular clay product or treated with finely ground clay and subsequently filtered.

A wide range of clay materials have been used for decolorizing. These may be substantially crude clay such as fuller's earth, which largely contains montmorillonite as the active clay ingredient, or specially treated attapulgites, montmorillonites, and kaolinites. Proprietary acid activation processes are frequently used for production of clay-derived materials of superior performance.

To be of value in an oil decolorizing operation, a relatively small amount of clay must reduce color substantially. Oil retention must be low, ie, only a small amount of oil is retained in the clay during the decolorization process. Further, the clay must be readily removed by filtration.

Because of the increasing popularity of cats as pets, a significant quantity of clay is being used in pet litter. Generally this material is attapulgite or montmorillonite based because these minerals have a high absorptive capacity for liquids and are readily granulated. Halloysite has also been used (19). Other applications for absorptive clays include cleaning up chemical spills and oil and grease removal from garage floors.

**Adhesives.** Clays, especially kaolin and attapulgite, are widely used in various adhesive formulations. Adhesives (qv) containing clays can be derived from natural products such as starch or protein, or be wholly synthetic, eg, latex, hot melt, emulsion, etc.

In addition to serving as an extender for the adhesive, the use of clay can also improve the properties of the system. The addition of clay to the adhesive can increase viscosity by reducing dripping and sagging, improve smoothness of the surface, and slow the penetration of the adhesive into the substrate thus reducing cost by lowering the adhesive requirement. Both air-floated and water-washed kaolins are used. The former is less costly, the latter is of better color and more uniform. Attapulgites are typically used to control viscosity and provide a thixotropic system for ease in handling.

**Catalysts.** Historically, crude clays have been used to some extent in petroleum refining (20). More recently, however, processed clays are increasingly used as raw materials and converted to more reactive catalyst products. Various proprietary processes are used and numerous patents have been issued.

Frequently kaolin clay is used for a raw material. In one of the older processes kaolin is treated with sulfuric acid at elevated temperature and subsequently washed to remove liberated alumina and alkalies. Kaolin can also serve as a raw material for preparing a number of synthetic zeolites (21).

**Cement.** Portland cement, a mixture of calcium silicate and calcium aluminate minerals, is produced by the calcination of argillaceous limestone or mixtures of limestone and clay (see CEMENT). Although other clays can be used, kaolin is preferred because of its alumina and silica content and low level of impurities. It is especially desirable in the manufacture of white cement and other types requiring careful control of chemical composition. Air-floated kaolin, because of its low cost, is usually used.

**Chemical Raw Material.** In addition to use as a catalyst raw material, clays are used or have been extensively studied as chemical raw material. For example, kaolin has been investigated as a raw material for aluminum metal production.



Kaolin has a 38 to 40% alumina content and is available in the United States in large quantities whereas the higher alumina bauxite reserves are very limited. The Bureau of Mines has actively carried out research in the aluminum from kaolin area for many years. Activity increases whenever imports of bauxite are threatened by war or other trade interruptions (1,22,23).

Kaolin, usually air-floated, is an essential ingredient in continuous filament fiber glass and significant quantities are used in this application (24).

**Inks.** Refined kaolin is a common ingredient in a large variety of printing inks (qv). In addition to extending the more expensive polymers present, kaolin also contributes to improved color strength, limits the penetration of the ink into the paper, controls rheology, and improves adhesion. Kaolin for this application must usually be as white as possible and free from oversize particles. Surface treated clays are used to improve compatibility with oil-based ink. Clays can also be an ingredient in the newer water-based or uv-cured inks.

**Pelletizing.** In many industries it is common practice to agglomerate fine-particle materials such as iron ores or fertilizers into larger, more easily handled aggregates. Bentonites of high dry strength are best suited for pelletizing because they provide a strong bond. Attapulgite can also be used.

**Pesticides.** Many pesticides are highly concentrated and are in a physical form requiring further treatment to permit effective application. Typically carriers or diluents are used (see INSECT CONTROL TECHNOLOGY). Although these materials are usually considered inert, they have a vital bearing on the potency and efficiency of the dust or spray because the carrier may consist of up to 99% of the final formulation. The physical properties of the carrier or diluent are of great importance in the uniform dispersion, the retention of pesticide by the plant, and in the preservation of the toxicity of the pesticide. The carrier must not, for example, serve as a catalyst for any reaction of the pesticide that would alter its potency.

Clays composed of attapulgite, montmorillonite, and kaolinite are used for pesticides in finely pulverized or granular form. Granular formulations are reportedly less expensive, more easily handled, reduce loss caused by wind drift, and produce a more effective coverage.

**Other Clay Uses.** Other applications for clays include use as a suspending agent, eg, montmorillonite and attapulgite in liquid fertilizers and dishwasher detergents; in pharmaceuticals (qv), eg, kaolinite and attapulgite for diarrhea control; in cosmetics, montmorillonite and attapulgite; and in water impendence where bentonite linings are used for reservoirs and waste disposal areas.

### Economic Aspects

Clays vary in price from only a few dollars per ton for common clay to >\$0.25/kg for some of the specialty surface treated clays. For clays that are used in large quantities such as kaolins for paper coatings, transportation to the point of use may be the primary cost component.

In the United States, kaolin is the principal clay product and about 9 million metric tons were reported mined and processed during 1991 (25). Bentonite production was reported as being 2 million tons for the same year. World production

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data for clays, often as a function of geographical location, use, or specific producer, are available (26).

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**CLINICAL CHEMISTRY.** See AUTOMATED INSTRUMENTATION,  
CLINICAL CHEMISTRY.

**CLUSTERS.** See SUPPLEMENT.

**CLUTCH FACINGS.** See BRAKE LININGS AND CLUTCH FACINGS.

**COAGULANTS AND ANTICOAGULANTS.** See BLOOD,  
COAGULANTS AND ANTICOAGULANTS.

## COAL

The use of coal, known as the rock that burns, was recorded in China, Greece, and Italy over 2000 years ago. Coal mining began in Germany around the tenth century AD and enough coal was mined in England for export in the thirteenth century. Coal mining began in the United States in about 1700.

Coal is usually a dark black color, although geologically younger deposits of brown coal have a brownish red color (see LIGNITE AND BROWN COAL). The color, luster, texture, and fracture vary with rank, type, and grade. Coal is the result of combined biological, chemical, and physical degradation of accumulated plant matter over geological ages. The relative amounts of remaining plant parts leads to different types of coal, which are sometimes termed banded, splint, nonbanded (cannel and boghead); or hard or soft; or lignite, subbituminous, bituminous, or